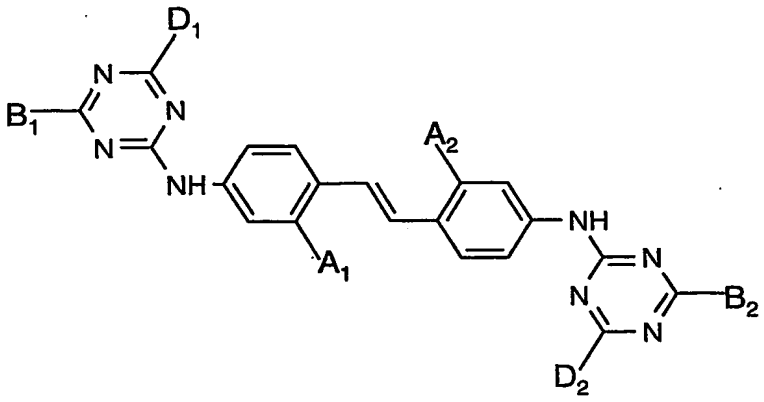
Amphoteric and Cationic Fluorescent Whitening Agents

The present invention relates to novel amphoteric and cationic bis-triazinylaminostilbene fluorescent whitening agents (FWA's), a process for their preparation and the use thereof for fluorescent whitening of synthetic or natural organic materials, in particular, paper.

The most commonly used types of fluorescent whitening agent for the fluorescent whitening of paper are those belonging to the class of di-, tetra- or hexasulphonic acid derivatives of bis-triazinylaminostilbenes, which are anionic in nature. Modern paper-making techniques, however, generally employ cationic polymers as assistants, for example, as retention agents or dewatering aids, in particular, during the preparation of recycling papers, which, most probably contain residual amounts of anionic FWA's. The presence of cationic polymers, however, results in quenching of the fluorescence of anionic FWA's, which is clearly disadvantageous. Consequently, there is a need for a type of FWA, which is not quenched by such polymers and, in addition is combinable with anionic FWA's.

Surprisingly, it has now been found that certain novel amphoteric and also cationic FWA's are detrimentally affected by the presence of cationic polymers nor by the presence of residual amounts of anionic FWA's and also exhibit excellent whitening properties when applied to paper.

Accordingly, the present invention provides novel compounds of the formula



(1),

wherein

A_1 and A_2 each, independently of one another, represent $-SO_3^-$ or $-SO_3M$, where

M represents hydrogen, an alkaline or alkaline earth metal, ammonium or alkyl ammonium,

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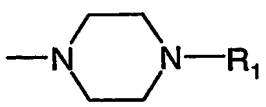
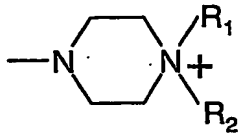
B_1 and B_2 each, independently of one another, represent the moiety

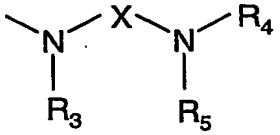
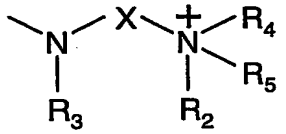
 (2) or  (3),

in which

R_1 represents hydrogen, a straight-chain C_1-C_{12}alkyl or branched C_3-C_{12}alkyl group which C_2-C_{12}alkyl and C_3-C_{12}alkyl group, respectively, may be interrupted by one or two heteroatoms and is unsubstituted or substituted by one or two -OH, -OC_1-C_4alkyl, -NH_2, -NHC_1-C_4alkyl, -N(C_1-C_4alkyl)$_2$, -N-pyrrolidino, -N-piperidino, -N-morpholino or -N^+(C_1-C_4alkyl)$_3$ groups and

R_2 represents C_1-C_4alkyl, C_2-C_4hydroxyalkyl, -CH_2CONH_2, -CH_2COOH or -CH_2COO C_1-C_4alkyl or, alternatively,

B_1 and B_2 each, independently of one another, represent a group of the formula

 (4) or  (5),

in which

R_3, R_4 and R_5 each, independently of each other, represent hydrogen, C_1-C_4alkyl, C_2-C_4hydroxyalkyl, the group -X'-NR_6R_7 or the group -X'-$N^+R_3R_6R_7$, whereby at least one of the substituents R_4 and/or R_5 represents -X'-NR_6R_7 or -X'-$N^+R_3R_6R_7$,

X and X' each, independently of each other, represent a straight-chain C_2-C_8alkylene or branched C_3-C_8alkylene chain, which is unsubstituted or substituted by one or two -OH or -C(=O)- groups,

R_6 and R_7 each, independently of each other, represent hydrogen, C_1-C_4alkyl or, together with the nitrogen atom to which they are bound, complete a pyrrolidino, piperidino or morpholino ring and

R_2 is as previously defined and each

D_1 and D_2, independently of one another, are either defined as for B_1 and B_2 or represent halogen, -NH_2, C_1-C_4monoalkyl- or dialkylamino, said alkyl groups being unsubstituted or substituted by C_1-C_4alkoxy, amino, mono- or di-C_1-C_4alkylamino or tri-C_1-C_4alkylammonium; C_2-C_4hydroxyalkylamino, C_2-C_4di(hydroxyalkyl)amino, anilino, an aniline monosulphonic acid or sulphonamide residue or a 5- or 6-membered, saturated heterocyclic ring or, alternatively, mixtures of compounds of formula (1).

Amphoteric compounds of formula (1) may exist either in the form of an internal or external salt. Thus, for example, in the case in which M in A_1 and /or A_2 represents hydrogen, compound (1) may exist as an equilibrium mixture of a neutral molecule and of a zwitterion, wherein A_1 and/or A_2 represent $-SO_3^-$, whilst the proton resides on the amine residues of substiuents B_1 and/or B_2, i.e. at least one of R_1 and R_2 in formula (3) and at least one of R_2, R_4 and R_5 in formula (5) represents hydrogen. Alternatively, such a compound may also be present in the form of an external salt, for example, where, in formula (1) A_1 and /or A_2 represents $-SO_3M$ and a proton resides on the amine residues of substiuents B_1 and/or B_2 as described above, a further anion An^- must also be present. In this case and also in the case of cationic derivatives carrying excess positive charge, the anion An^- is a colourless anion derived from an inorganic or from an organic acid.
Typical examples of such anionic radicals include halide, e.g. chloride, bromide or iodide, sulphate, methyl sulphate, boron tetrafluoride, aminosulphonate, perchlorate, carbonate, bicarbonate, phosphate, phosphoromolybdate, phosphorotungstate, phosphorotungstomolybdate, benzenesulphonate, naphtalenesulphonate, 4-chloro-benzenesulphonate, oxalate, maleate, acetate, propionate, lactate, monochloroacetate, tartrate, methanesulphonate or benzoate. Preferable examples of anions are chloride, hydrogensulphate, sulphate, methosulphate, phosphate, formate, lactate or acetate, especially chloride and methosulphate. The anion can be exchanged in a known manner for another anion.

One class of preferred compounds of formula (1) is that in which the residues A_1 and A_2 are identical, B_1 and B_2 are identical and D_1 and D_2 are identical and, more particularly, compounds of formula (1) in which the moieties
B_1 and/or B_2 are represented by the formulae (2) and/or (3) and in which
R_1 represents hydrogen, a straight-chain C_1-C_4alkyl or branched C_3-C_4alkyl group which may be interrupted by one or two heteroatoms and is unsubstituted or substituted by one or two -OH, $-OC_1$-C_4alkyl, $-NH_2$, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, -N-pyrrolidino, -N-piperidino, -N-morpholino or $-N^+(C_1$-C_4alkyl$)_3$ groups,
A_1 and A_2 are both $-SO_3^-$ or $-SO_3M$,
M, R_2, D_1 and D_2 being as previously defined.

Compounds of formula (1), which are of especial interest, are those in which the moieties

B_1 and B_2 are identical and represented by the formulae (2) or (3), whereby
R_1 represents hydrogen, a straight-chain C_1-C_4alkyl or branched C_3-C_4alkyl group which may be unsubstituted or substituted by one or two -OH, -OC_1-C_4alkyl, -NH_2, -NHC_1-C_4alkyl, -N(C_1-C_4alkyl)$_2$, -N-pyrrolidino, -N-piperidino, -N-morpholino or -N^+(C_1-C_4alkyl)$_3$ group,
R_2 represents C_1-C_4alkyl,
A_1 and A_2 are both -SO_3^- or -SO_3M, whereby
M represents hydrogen, potassium or sodium and
D_1 and D_2 are identical and may be represented by halogen, especially chlorine, C_1-C_4monoalkyl- or dialkylamino, said alkyl groups being unsubstituted or substituted by mono- or di-C_1-C_4alkylamino or tri-C_1-C_4alkylammonium; C_2-C_4hydroxyalkylamino, C_2-C_4-di(hydroxyalkyl)amino, anilino, an aniline sulphonamide residue or a morpholino-, piperidino- or -N-C_1-C_4substituted piperazino ring.

Most especially preferred compounds of formula (1), in which B_1 and B_2 are identical and represented by the formulae (2), are those in which
R_1 represents hydrogen, a straight-chain C_1-C_4alkyl, especially methyl, ethyl or n-propyl, or branched C_3-C_4alkyl group which may be unsubstituted or substituted by one -OH, for example hydroxyethyl or hydroxypropyl, -N(C_1-C_4alkyl)$_2$, especially dimethyl- or diethylamino, -N-pyrrolidino, or -N^+(C_1-C_4alkyl)$_3$ group, or by one -OH group and one -N^+(C_1-C_4alkyl)$_3$ group, for example, 3-trimethylammonium-2-hydroxy-1-propyl,
A_1 and A_2 are both -SO_3^- or -SO_3M, whereby
M represents hydrogen, potassium or sodium and
D_1 and D_2 are identical and may be represented by chlorine, C_1-C_4monoalkyl-, for example methyl-, ethyl or propylamino, or dialkylamino, for example dimethyl or diethylamino, said alkyl groups being unsubstituted or substituted by di-C_1-C_4alkylamino, for example dimethylaminopropylamino, or tri-C_1-C_4alkylammonium, for example trimethylammoniumpropylamino; C_2-C_4hydroxyalkylamino, especially hydroxyethyl or hydroxypropyl, C_2-C_4-di(hydroxyalkyl)amino, in particular, diethanolamino, anilino, an aniline 4-sulphonamide residue or a morpholino-, or -N-C_1-C_4substituted piperazino, for example an N-methyl piperazino, ring.

Most especially preferred compounds of formula (1), in which B_1 and B_2 are identical and represented by the formulae (3), are those in which
R_1 represents hydrogen, methyl, ethyl or hydroxyethyl,

R_2 represents hydrogen, methyl or ethyl,
A_1 and A_2 are both $-SO_3^-$ or $-SO_3M$, whereby
M represents hydrogen, potassium or sodium and
D_1 and D_2 are identical and may be represented by dimethylaminopropylamino, trimethylammoniumpropylamino; C_2-C_4hydroxyalkylamino, diethanolamino, anilino, an aniline 4-sulphonamide residue or a morpholino-, or -N-C_1-C_4substituted piperazino, for example an N-methyl piperazino or an N,N-dimethylpiperazinium, ring.

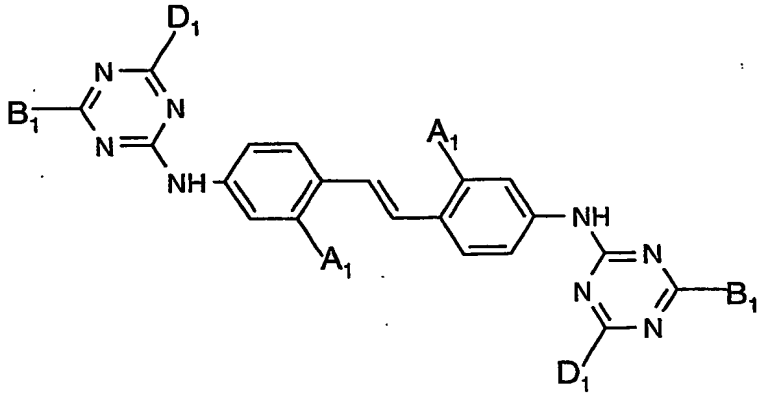
A further class of preferred compounds of formula (1) is that in which the residues A_1 and A_2 are identical, B_1 and B_2 are identical and D_1 and D_2 are identical and, more particularly, compounds of formula (1) in which the moieties
B_1 and/or B_2 are represented by the formulae (4) and/or (5), whereby
R_4 represents the group $-X'-NR_6R_7$ or the group $-X'-N^+R_3R_6R_7$,
X and X' each, independently of each other, represent a straight-chain C_2-C_8alkylene or branched C_3-C_8alkylene chain, which is unsubstituted or substituted by one or two -OH or -C(=O)- groups,
R_3 and R_5 each, independently of each other, represent hydrogen, C_1-C_4alkyl or C_2-C_4hydroxyalkyl,
R_6 and R_7 each, independently of each other, represent hydrogen, C_1-C_4alkyl or, together with the nitrogen atom to which they are bound, complete a pyrrolidino, piperidino or morpholino ring,
A_1 and A_2 are both $-SO_3^-$ or $-SO_3M$,
M, R_2, D_1 and D_2 being as previously defined.

More especially preferred are compounds of formula (1) in which the moieties
B_1 and B_2 are identical and represented by the formulae (4) or (5) are those in which
R_4 represents the group $-X'-NR_6R_7$ or the group $-X'-N^+R_3R_6R_7$,
X and X' each, independently of each other, represent a C_2-C_4alkylene chain, which is unsubstituted or substituted by -OH,
R_3 and R_5 each, independently of each other, represent hydrogen or C_1-C_4alkyl,
R_6 and R_7 each, independently of each other, represent hydrogen, C_1-C_4alkyl or, together with the nitrogen atom to which they are bound, complete a pyrrolidino, piperidino or morpholino ring,
R_2 represents C_1-C_4alkyl,

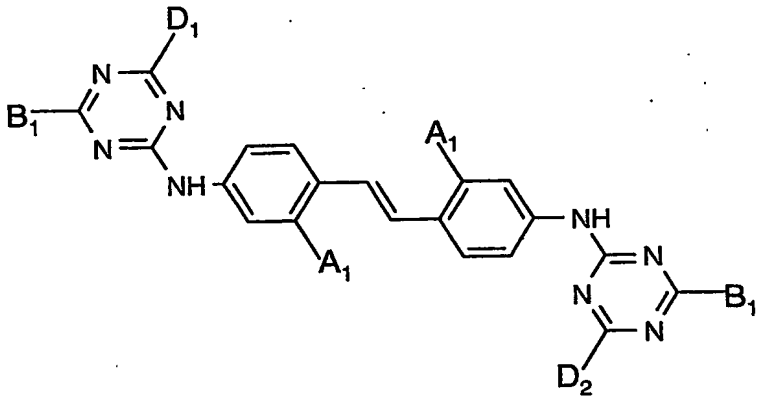
A_1 and A_2 are both $-SO_3^-$ or $-SO_3M$, whereby
M represents hydrogen, potassium or sodium and
D_1 and D_2 are identical and may be represented by halogen, especially chlorine, C_1-C_4monoalkyl- or dialkylamino, said alkyl groups being unsubstituted or substituted by mono- or di-C_1-C_4alkylamino or tri-C_1-C_4alkylammonium; C_2-C_4hydroxyalkylamino, C_2-C_4-di(hydroxyalkyl)amino, anilino, an aniline sulphonamide residue or a morpholino-, piperidino- or -N-C_1-C_4alkylsubstituted piperazino ring, an anilino residue being preferred.

Most especially preferred are compounds of formula (1) in which the moieties
B_1 and B_2 are identical and represented by the formulae (4) or (5) are those in which
R_4 represents the group $-X'-NR_6R_7$ or the group $-X'-N^+R_3R_6R_7$,
X and X' each, independently of each other, represent a propylene chain, which is unsubstituted or substituted by -OH,
R_3 and R_5 each, independently of each other represent hydrogen or methyl,
R_6 and R_7 each represent methyl,
R_2 represents methyl,
A_1 and A_2 are both $-SO_3^-$ or $-SO_3M$, whereby
M represents hydrogen, potassium or sodium and
D_1 and D_2 are identical and represent either an anilino or aniline-4-sulphonamido residue.

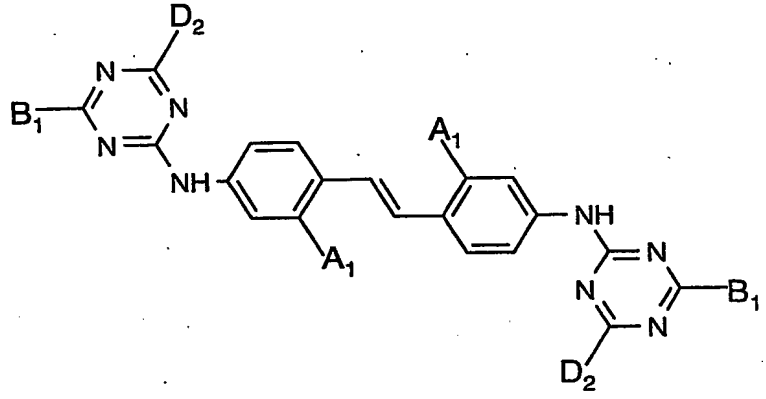
Alternatively, one further preferred aspect of the invention relates to a three-component mixture of compounds of formula (1), comprising two symmetrical components, i.e. compounds of formula (1) in which the residues A_1 and A_2 are identical, B_1 and B_2 are identical and D_1 and D_2 are identical, and a third component in which the residues A_1 and A_2 are identical, but either, B_1 and B_2 are different or D_1 and D_2 are different, which, preferably, may be illustrated by the following formulae (1a), (1b) and (1c):



(1a)



(1b)



(1c),

wherein A_1, B_1, D_1 and D_2 and also the preferences thereof are as previously described. Most preferred mixtures, however, are those in which A_1 represents $-SO_3H$, B_1 represents a 4-(2-hydroxyethyl)piperazin-1-yl residue, D_1 is anilino and D_2 is either a morpholino or a 2-hydroxypropylamino residue.

Within the scope of the definitions of the substituents R_1, R_2, R_3, R_4, R_5, R_6 and/or R_7, straight-chain C_1-C_{12}alkyl groups are, for example, methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, and n-dodecyl, whilst branched C_3-C_{12}alkyl groups are, for example, isopropyl, sec-butyl, isobutyl, t-butyl, 2-ethylbutyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, 1-methylhexyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, 1-methylundecyl and 1,1,3,3,5,5-hexamethylhexyl. Where the C_2-C_{12}alkyl group is interrupted by heteroatoms, these may be sulphur, nitrogen or, especially, oxygen, whilst C_2-C_4hydroxyalkyl may be hydroxyethyl, hydroxy-n- or isopropyl or hydroxybutyl.

A C_2-C_8alkylene chain, in the definitions of X and X', may, for example be an ethylene, n-propylene, methyl ethylene, 1- or 2-methylpropylene, n-butylene, ethylethylene, n-pentylene, ethyl propylene, dimethyl propylene, methyl butylene, n-hexylene, dimethyl butylene, methyl pentylene, ethyl butylene, n-heptylene, methyl hexylene, dimethyl pentylene, ethyl pentylene, trimethyl butylene, n-octylene, methyl heptylene, dimethyl or ethyl hexylene or a trimethyl heptylene chain.

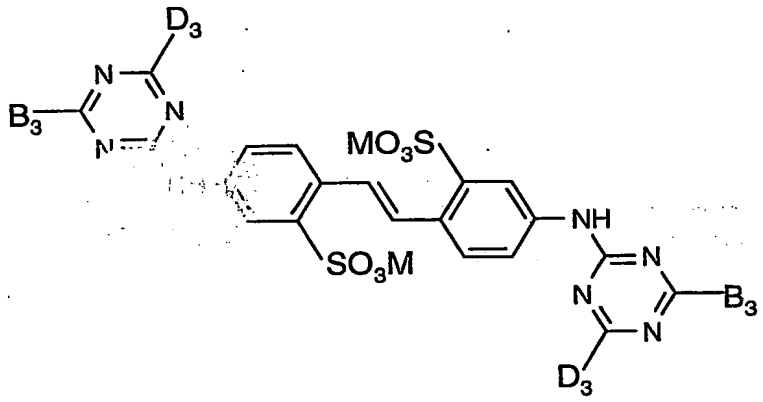
Within the scope of the definitions of D_1 and D_2 in formula (1), halogen is iodine, bromine, fluorine or, especially, chlorine, whilst C_1-C_4monoalkyl- or dialkylamino may be, for example, mono- or dimethylamino, mono- or diethylamino, mono- or dipropyl- or butylamino. Tri-C_1-C_4alkylammonium is, for example, trimethylammonium, ethyl dimethylammonium, triethylammonium, methyl diethylammonium, tripropyl or tributylammonium, whilst C_2-C_4hydroxyalkylamino and C_2-C_4di(hydroxyalkyl)amino may be, for example, ethanolamino, diethanolamino, propanolamino, dipropanolamino, hydroxybutylamino or di(hydroxybutyl)amino and a 5- or 6-membered, saturated heterocyclic ring is, for example, pyrrolidino, morpholino, piperidino or piperazino.

Where M represents an alkaline or alkaline [illegible], this may be lithium, potassium, sodium, calcium or magnesium, whilst alkyla[illegible]may be ammonium which is mono-, di-, tri- or tetrasubstituted by C_1-C_4alkyl or C_2-C_4hydroxyalkyl or a mixture thereof.

The compounds of formula (1) of the invention may be prepared by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'-disulphonic acid, an amino compound capable of introducing groups B_1 and/or B_2 or precursors thereof and an amino compound capable of introducing groups D_1 and/or D_2 or precursors thereof, B_1, B_2, D_1 and D_2 being as previously defined. The mixtures of compounds of the invention may be obtained purely by mechanical mixing of the individual components or, preferably, from the synthesis by employing mixtures of amino compounds capable of introducing groups B_1 and/or B_2 or precursors thereof and or mixtures of amino compounds capable of introducing groups D_1 and/or D_2 or precursors thereof.

In certain cases it may be advantageous to firstly produce an intermediate compound by way of the above reaction sequence, which is subsequently further reacted to result in the compound of formula (1). Thus, for example, a compound of formula (1) in which B_1 and/or B_2 is represented by formula (3) may be obtained by firstly preparing the corresponding

compound in which B_1 and/or B_2 is represented by formula (2) and subsequent reaction with a compound capable of introducing the group R_2. Similarly, a compound of formula (1) in which B_1 and/or B_2 is represented by formula (5) may be obtained from the corresponding compound in which B_1 and/or B_2 is represented by formula (4). Furthermore, such compounds may also be obtained from the corresponding amine precursors by treatment with suitable reactants capable of introducing any one of the groups R_1-R_5. Suitable reactants are, for example, alkylating or quaternising agents such as dimethyl or diethyl sulphate, chloro or bromoacetic acids, esters or amides, appropriate alkyl chlorides, bromides or iodides or compounds capable of introducing the group -X'-NR_6R_7 or -X'-$NR_3R_6R_7$ such as 3-chloro-2-hydroxy-1,1,1-trimethyl propylammonium chloride or with analogous compounds. In this respect, certain compounds designated above as intermediates are novel and, as a consequence, a further aspect of the invention are compounds of the formula



(6),

wherein

B_3 represents a group of the formula -$NH(CH_2)_nNR_8R_9$, n being 2, 3 or 4 and

D_3 represents halogen, an anilino, anilino-sulphonic acid or anilino-sulphonamide residue,

R_8 and R_9 each. Independently of each other, represent hydrogen, C_1-C_4alkyl, C_2-C_4-hydroxyalkyl or, together with the nitrogen atom to which they are bound, complete a pyrrolidino, piperidino or morpholino ring and M, is as defined in claim 1, with the proviso that those compounds in which D_3 is anilino, B_3 is an N-(3-aminopropyl)-diethanolamino, N,N-dimethyl-1,3-propanediamino or 4-(3'-aminopropyl)morpholine residue or in which D_3 represents a sulphanilamide residue and B_3 is a 4-(3'-aminopropyl)morpholine residue and M is hydrogen are excluded, which are useful as intermediates for the preparation of compounds of formula (1).

Compounds of formula (6), which are of special interest, are those in which

B_3 represents a group of the formula -$NH(CH_2)_3NHR_8R_9$,

D_3 represents an anilino or anilino-4-sulphonamide residue,
M represents hydrogen or sodium and
R_8 and R_9 are hydrogen or C_1-C_4alkyl, preferably hydrogen.

The compounds of formula (6) of the invention may be similarly prepared by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'-disulphonic acid, an amino compound capable of introducing groups B_3 and an amino compound capable of introducing groups D_3, B_3 and D_3 being as previously defined.

All starting materials are known compounds, which are readily available or may be prepared by known methods.

A further aspect of the invention is a composition for whitening synthetic or natural organic materials, which contains water, a fluorescent whitening agent of formula (1) or mixtures thereof and, optionally, auxiliaries.

More specifically, such brightener compositions contain water and, in each case based on the weight of the formulation, from 3 to 25% by weight, preferably from 5 to 15% by weight of the above defined fluorescent whitening agent mixture and also 0 to 60%, preferably 5 to 50% by weight, of auxiliaries.

Suitable auxiliaries include, for example, anionic or non-ionic dispersants from the class of ethylene oxide adducts with fatty alcohols, higher fatty acids or alkyl phenols or ethylenediamine ethylene oxide-propylene oxide adducts, copolymers of N-vinylpyrrolidone with 3-vinylpropionic acid, water retention aids, such as ethylene glycol, glycerol or sorbitol, or biocides.

Most of the compounds of formula (1) and their mixtures are excellent fluorescent whitening agents for substrates such as textiles, for the addition to detergent compositions and, especially for the fluorescent whitening of paper.

Accordingly, the present invention further provides a method for the fluorescent whitening of a substrate comprising contacting the substrate with a compound having the formula (1) or mixtures of compounds.

When used for the fluorescent whitening of paper, the compound of formula (1) and the mixtures according to the present invention may be applied to the paper substrate in the pulp mass, in the form of a paper coating composition, or directly in the size press or metering press.

In one preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface, comprising contacting the paper surface with a coating composition comprising a white pigment; a binder dispersion; optionally a water-soluble co-binder; and sufficient of a fluorescent whitening agent having the formula (1) or mixtures thereof according to the present invention, to ensure that the treated paper contains 0.01 to 1 % by weight, based on the white pigment, of a fluorescent whitening agent having the formula (1).

As the white pigment component of the paper coating composition used according to the method of the present invention, there are preferred inorganic pigments, e.g., aluminium or magnesium silicates, such as China clay and kaolin and, further, barium sulfate, satin white, titanium dioxide, calcium carbonate (chalk) or talcum; as well as white organic pigments.

The paper coating compositions used according to the method of the present invention may contain, as binder, inter alia, plastics dispersions based on copolymers of butadiene/styrene, acrylonitrile/butadiene/styrene, acrylic acid esters, acrylic acid esters/styrene/acrylonitrile, ethylene/vinyl chloride and ethylene/vinyl acetate; or homopolymers, such as polyvinyl chloride, polyvinylidene chloride, polyethylene and polyvinyl acetate or polyurethanes. A preferred binder consists of styrene/butyl acrylate or styrene/butadiene/ acrylic acid copolymers or styrene/butadiene rubbers. Other polymer lattices are described, for example, in U.S.Patent Specifications 3,265,654, 3,657,174, 3,547,899 and 3,240,740.

The optional water-soluble protective colloid may be, e.g., soya protein, casein, carboxymethylcellulose, natural or modified starch, chitosan or a derivative thereof or, especially, polyvinyl alcohol. The preferred polyvinyl alcohol protective colloid component may have a wide range of saponification levels and molecular weights; e.g. a saponification level ranging from 40 to 100; and an average molecular weight ranging from 10,000 to 100,000.

Recipes for coating compositions for paper are described, for example, in J.P. Casey "Pulp and Paper"; Chemistry and Chemical Technology, 2nd edition, Volume III, pages1684-1649 and in "Pulp and Paper Manufacture", 2nd and 5th edition, Volume II, page497 (McGraw-Hill).

The paper coating compositions used according to the method of the present invention preferably contain 10 to 70% by weight of a white pigment. The binder is preferably used in an amount, which is sufficient to make the dry content of polymeric compound up to 1 to 30%, by weight, preferably 5 to 25% by weight, of the white pigment. The amount of fluorescent brightener preparation used according to the invention is calculated so that the fluorescent brightener is preferably present in amounts of 0.01 to 1% by weight, more preferably 0.05 to 1% by weight, and especially 0.05 to 0.6% by weight, based on the white pigment.

The paper coating composition used in the method according to the invention can be prepared by mixing the components in any desired sequence at temperature from 10 to 100°C, preferably 20 to 80°C. The components here also include the customary auxiliaries, which can be added to regulate the rheological properties, such as viscosity or water retention capacity, of the coating compositions. Such auxiliaries are, for example, natural binders, such as starch, casein, protein or gelatin, cellulose ethers, such as carboxyalkylcellulose or hydroxyalkylcellulose, alginic acid, alginates, polyethylene oxide or polyethylene oxide alkyl ethers, copolymers of ethylene oxide and propylene oxide, polyvinyl alcohol, water-soluble condensation products of formaldehyde with urea or melamine, polyphosphates or polyacrylic acid salts.

The coating composition used according to the method of the present invention is preferably used to produce coated printed or writing paper, or special papers such as ink-jet or photographic papers, or cardboard.

The coating composition used according to the method of the invention can be applied to the substrate by any conventional process, for example with an air blade, a coating blade, a roller, a doctor blade or a rod, or in the size press, after which the coatings are dried at paper surface temperatures in the range from 70 to 200°C, preferably 90 to 130°C, to a residual moisture content of 3-8%, for example with infra-red driers and/or hot-air driers. Comparably high degrees of whiteness are thus achieved even at low drying temperatures.

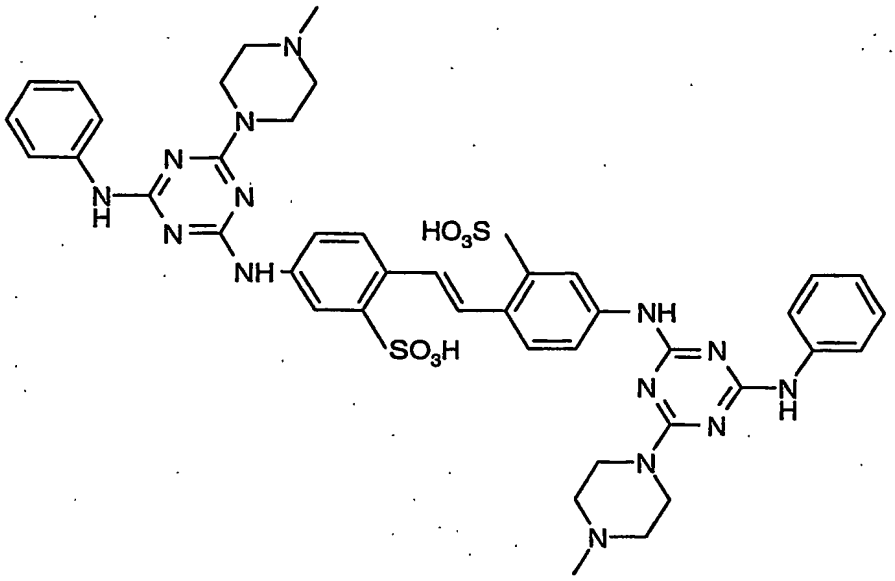
By the use of the method according to the invention, the coatings obtained are distinguished by optimum distribution of the dispersion fluorescent brightener over the entire surface and by an increase in the level of whiteness thereby achieved, by a high fastness to light and to elevated temperature (e.g. stability for 24 hours at 60-100°C.) and excellent fastness to water.

In a second preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface comprising contacting the paper in the size press with an aqueous solution containing a size, optionally an inorganic or organic pigment and 0.1 to 20g/l of a fluorescent whitening agent having the formula (1) or mixtures thereof. Preferably, the size is starch, a starch derivative or a synthetic sizing agent, especially a water-soluble copolymer.

The compounds and mixtures of compounds of the present invention are particularly advantageous in that they exhibit not only extremely high whitening ability, also in the presence of cationic polymers or residual amounts of anionic FWA's, but, in addition, in many cases highly desirable water solubilities and fastness properties.

The following Examples serve to illustrate the invention without intending to be restrictive in nature; parts and percentages are by weight, unless otherwise stated.

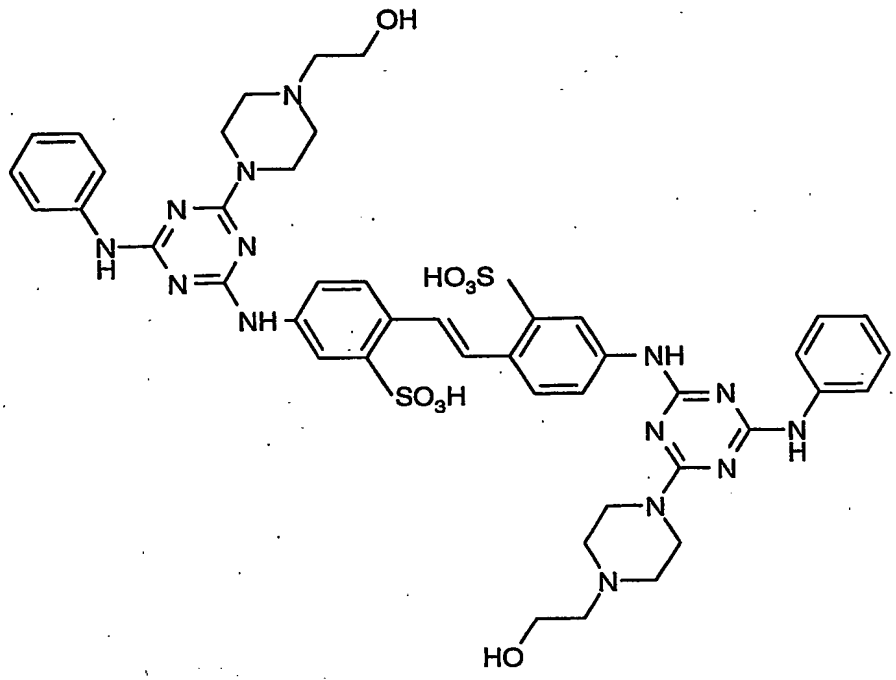
Example 1



(101)

To 24.0g of 1-methylpiperazine previously heated to 90°C are added 8.2g of 4,4'-bis [(4-[illegible]-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt with [illegible]. The temperature rises to 115°C and a cloudy solution results. After stirring for 90 minutes at 115-120°C and then cooling, 25ml of water are added and the resulting solution evaporated to dryness under vacuum. The product is suspended in 150ml of water, the pH adjusted to 1 and the mixture stirred for 2 hours. After standing overnight, the product is filtered, washed with 5% sodium chloride solution and dried under vacuum at 70°C. There are obtained 9.0g of the compound of formula (101) as yellow crystals.

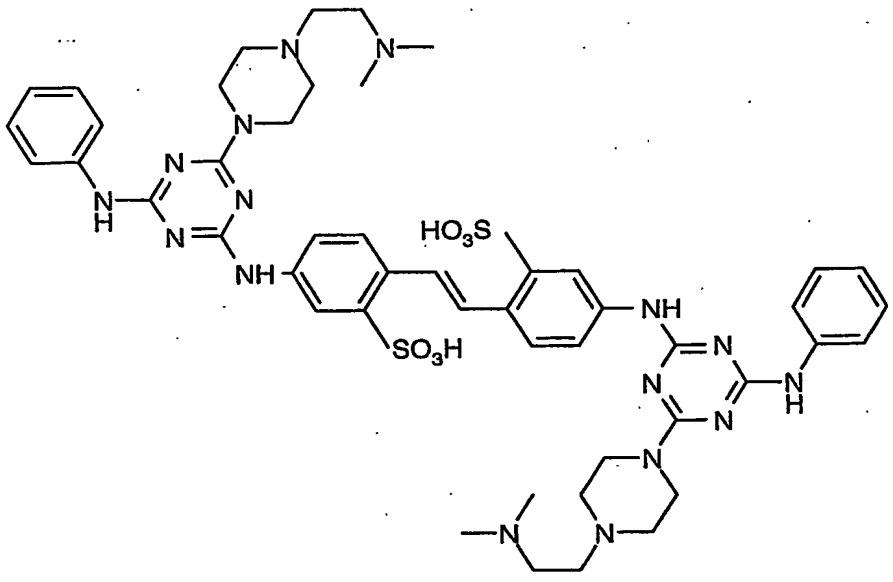
Example 2



(102)

By proceeding in a manner analogous to that described in Example 1, but replacing 1-methylpiperazine by an equivalent quantity of N-(2-hydroxyethyl)piperazine, the compound of formula (102) is obtained.

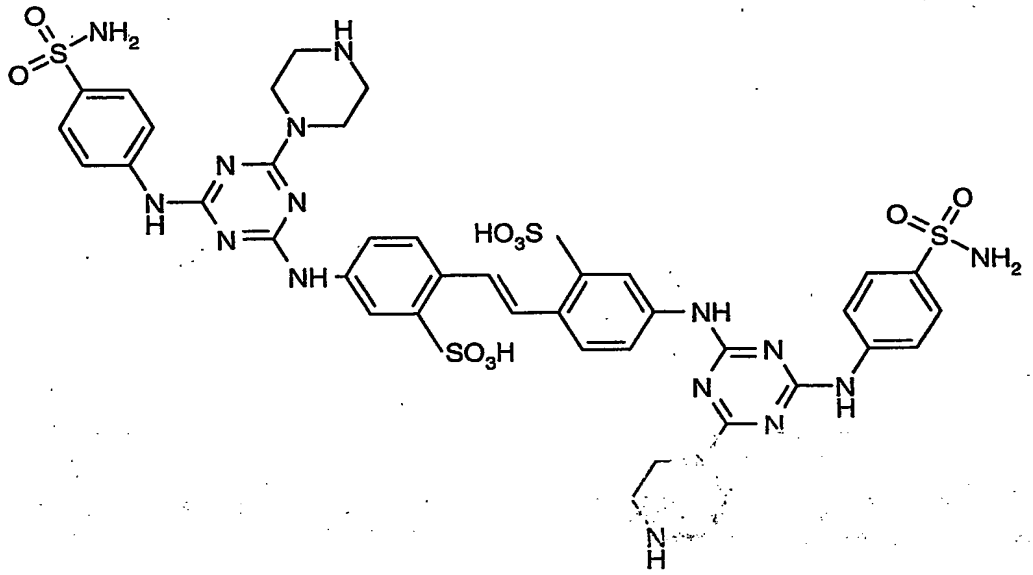
Example 3



(103)

By proceeding in a manner analogous to that described in Example 1, but replacing the 1-methylpiperazine by an equivalent quantity of 1-(2-dimethylaminoethyl)piperazine, the compound of formula (103) is obtained.

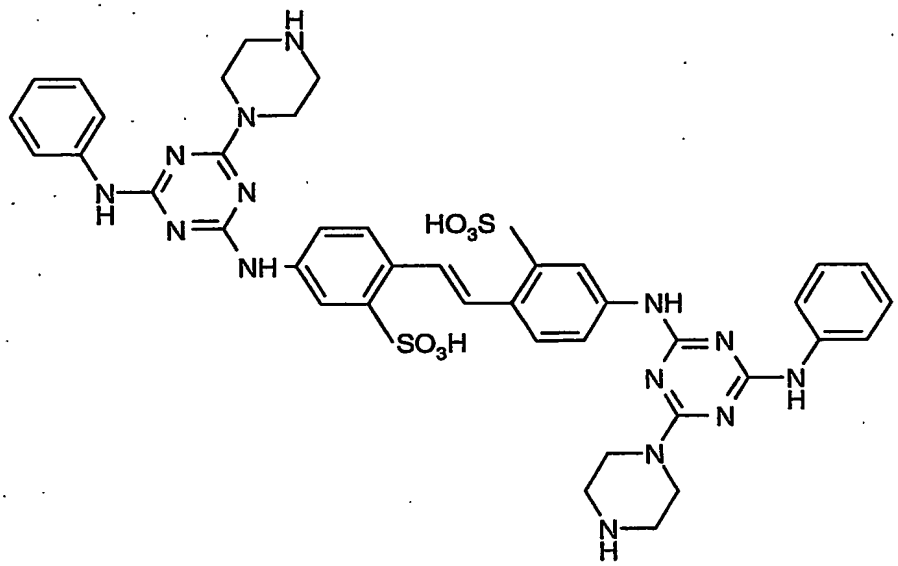
Example 4



(104)

30g of piperazine are dissolved in 200ml of water at 80°C under an atmosphere of nitrogen. To the resulting stirred solution, there are added 39.0g of 4,4'-bis [(4-p-sulphonamidoanilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt at 85-90°C over 1 hour. After stirring for a further 90 minutes, the solution is cooled to 70°C and the pH adjusted to 5 by addition of 40ml of concentrated hydrochloric acid. The precipitate is filtered, washed with water and resuspended in 300ml of water. After warming to 80°C, 7ml of 50% sodium hydroxide solution are added, whereby the pH rises to 10 and a solution results. The solution is cooled, the pH adjusted to 5 by addition of 18ml of 17% aqueous hydrochloric acid and the yellow crystalline precipitate filtered off, washed with water and dried under vacuum at 70°C. There are obtained 34.4g of the compound of formula (104) as yellow crystals.

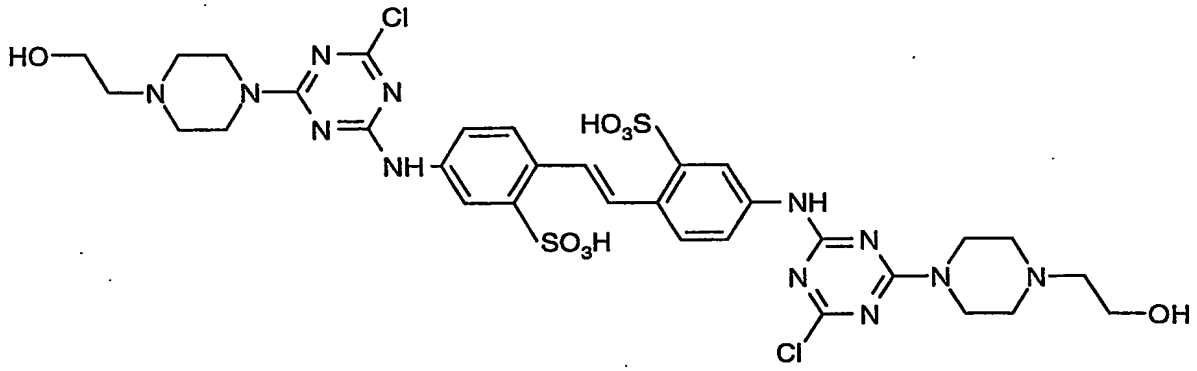
Example 5



(105)

By proceeding in a manner analogous to that described in Example 4, but replacing the 4,4'-bis [(4-p-sulphonamidoanilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt by an equivalent quantity of 4,4'-bis [(4-anilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt, the compound of formula (105) is obtained.

Example 6

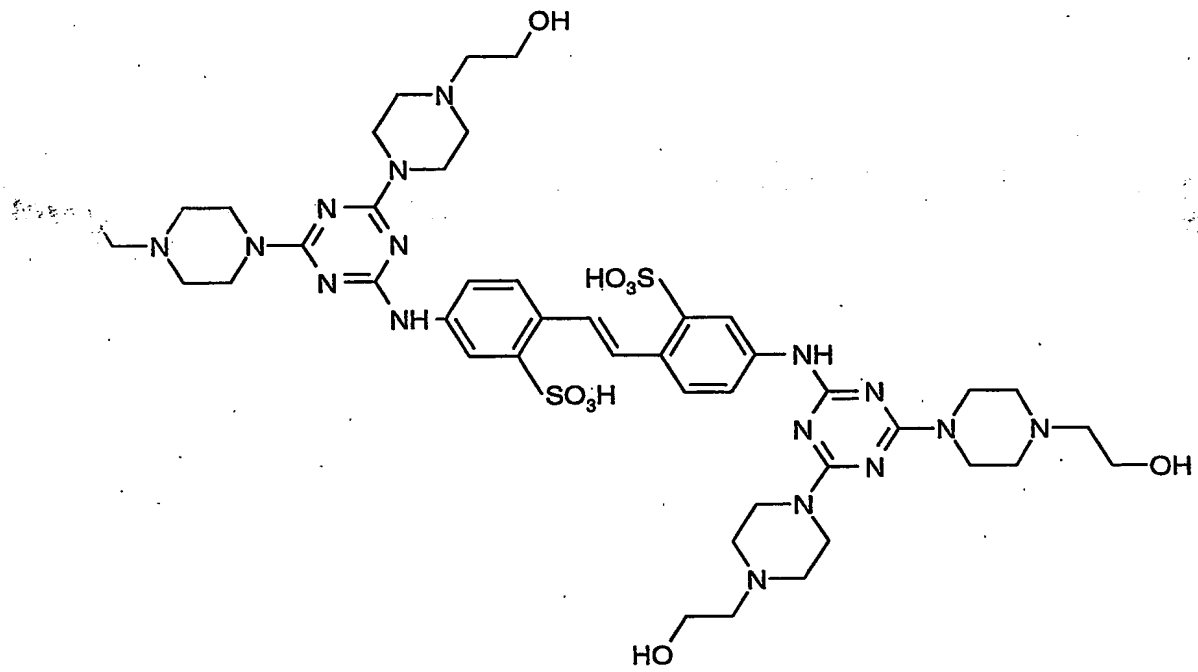


(106

A solution of 120g of cyanuric chloride in 930ml of methyl ethyl ketone is added with stirring to 400g of ice water, with cooling, at 5-10°C. 996ml of an aqueous solution containing 12g of 4,4'-diaminostilbene-2,2'-disulphonic acid and 2.5g of sodium carbonate per 100ml are then added dropwise during 70 minutes, with stirring, at 5-10°C, the pH being maintained at

4.5-5.5 by addition of aqueous sodium carbonate solution containing 20g of sodium carbonate per 100ml. Following the addition, the mixture is stirred for a further 10 minutes at 5-10°C and then treated dropwise with 86.3g of N-(2-hydroxyethyl)piperazine during 10 minutes when the pH rises to 8.7 and the temperature to 18°C. The resulting viscous yellow suspension is then warmed to 72°C over 1 hour and stirring continued at this temperature for a further 2 hours. The temperature is then raised to 85°C and the methyl ethyl ketone distilled off. The mixture is then cooled to 50°C, allowed to stand overnight, then filtered and washed with 500ml of water, then with 500ml of 5% aqueous sodium chloride. After drying at 70°C under vacuum, there are obtained 295.7g of the compound of formula (106) as yellow crystals.

Example 7

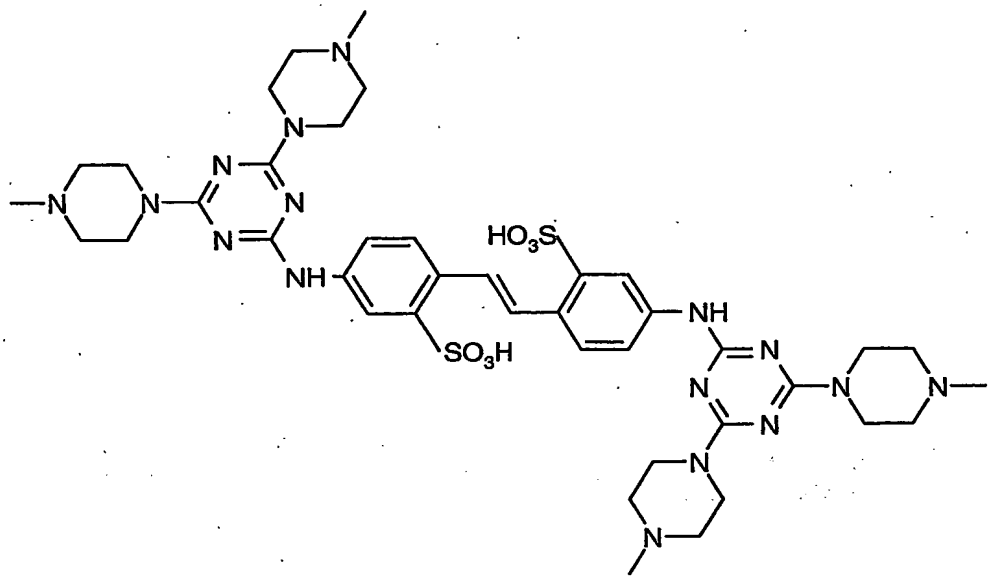


(107

The procedure of Example 5 is repeated, but prior to distillation of the methyl ethyl ketone, 102g of N-(2-hydroxyethyl)piperazine are added dropwise to the suspension over 15 minutes. The reaction mixture is warmed to 85°C. The pH is adjusted to 8.0-8.5 by addition of an aqueous sodium hydroxide solution containing 50g of sodium hydroxide per 100ml and the methyl ethyl ketone distilled off over 90 minutes. During this time the temperature is raised to 97°C and the mixture stirred for a further 90 minutes at this temperature, the pH

being maintained between 8.0 and 8.5 by further addition of aqueous sodium hydroxide. The reaction mixture is cooled to 60°C, filtered with suction and washed with 5% aqueous sodium chloride solution. After drying at 70°C under vacuum, there are obtained 369g of the compound of formula (107) as a yellowish white solid.

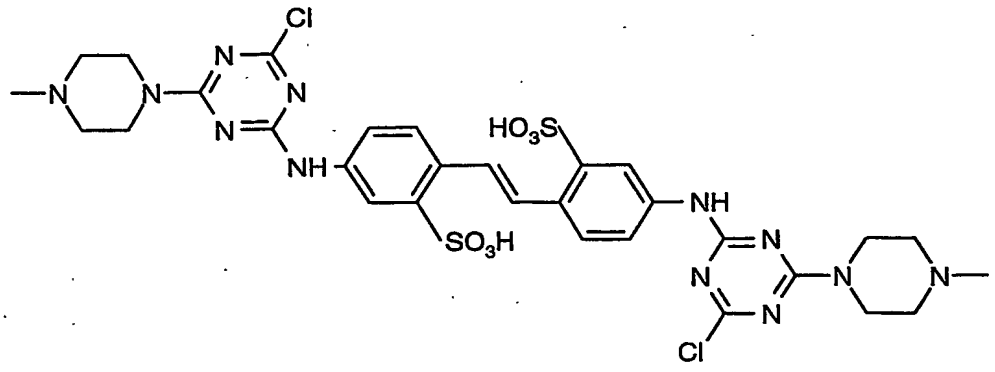
Example 8



(108)

By following the procedure described in Example 7, but replacing the N-(2-hydroxyethyl)-piperazine by an equivalent quantity of N-methylpiperazine, there are obtained 255.3g of the compound of formula (108) as yellow crystals.

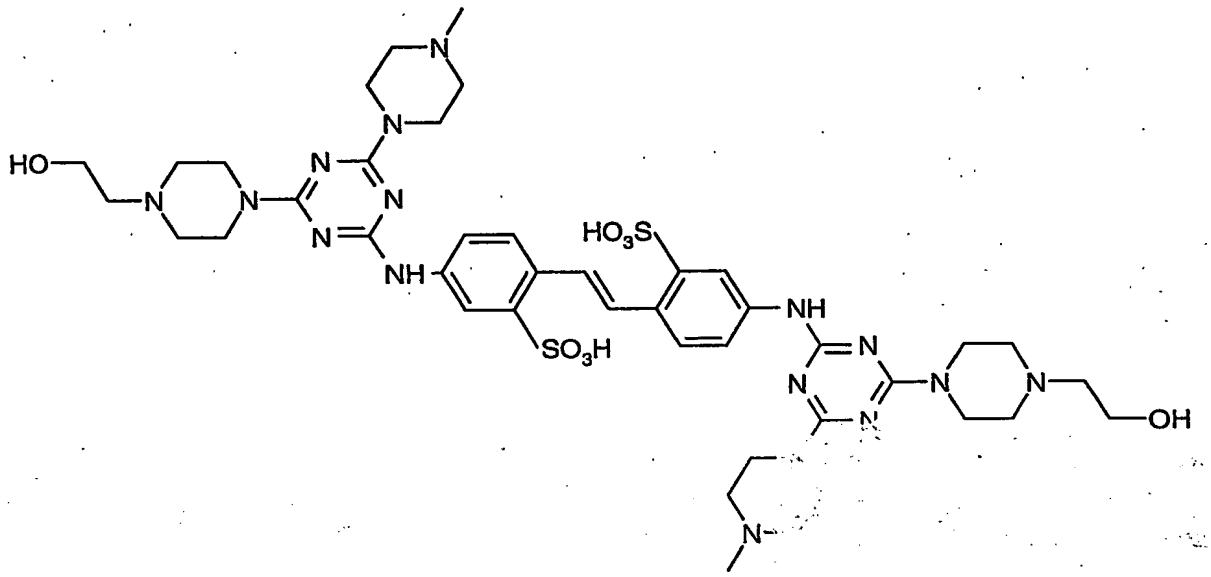
Example 9



(109)

By following the procedure described in Example 6, but replacing the N-(2-hydroxyethyl)-piperazine by an equivalent quantity of N-methylpiperazine, there are obtained 246.3g of the compound of formula (109) as yellow crystals with an active content of 92.9%.

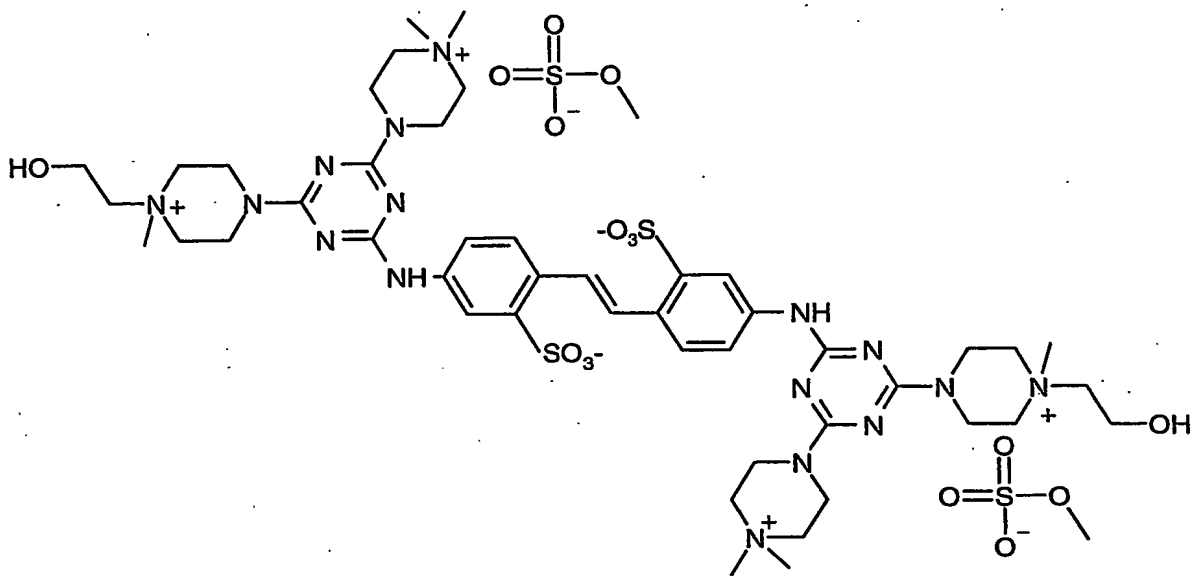
Example 10



(110)

To 45.1g of N-methylpiperazine previously heated to 80°C, 24.2g of the compound of formula (106) are added with stirring over 15 minutes. The temperature is then raised to 115-120°C and the yellowish brown solution stirred for a further 4 hours at this temperature. After cooling the mixture is diluted with 100ml of water and the resulting solution evaporated to dryness on a rotary evaporator. This procedure is repeated twice, the residue dissolved in 250ml of water, the pH adjusted to 1 by addition of concentrated hydrochloric acid, filtered at pH 4.5 and the filter residue washed with 5% sodium chloride solution. After drying at 70°C under vacuum, there are obtained 27.6g of the compound of formula (110) as yellowish brown crystals.

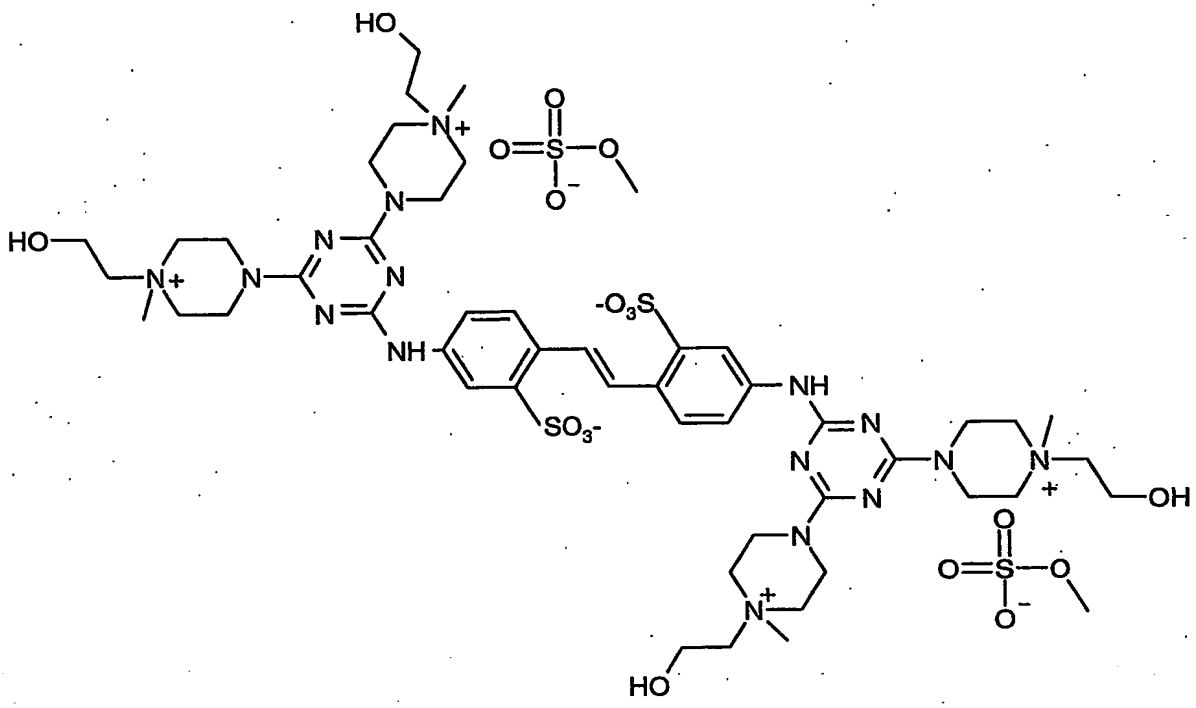
Example 11



(111)

To a mixture of 120ml of water and 2N aqueous sodium hydroxide solution, 14.0g of the compound of formula (111) are added with stirring at 40°C. The mixture is warmed to 80°C and the resulting solution then cooled to 45°C and treated with 15.1g of dimethyl sulphate over 1-2 minutes. Following the addition, the solution is stirred for 45 minutes at 48°C, the pH being maintained at 10.5-11.0 by addition of a total of 35ml of 2N aqueous sodium hydroxide solution. The temperature is then raised to 60°C, the mixture stirred for a further 45 minutes at this temperature and then allowed to stand. The reaction mixture is evaporated on a rotary evaporator and the residue dried under vacuum at 70°C to yield 17.4g of the compound of formula (111) as yellow crystals.

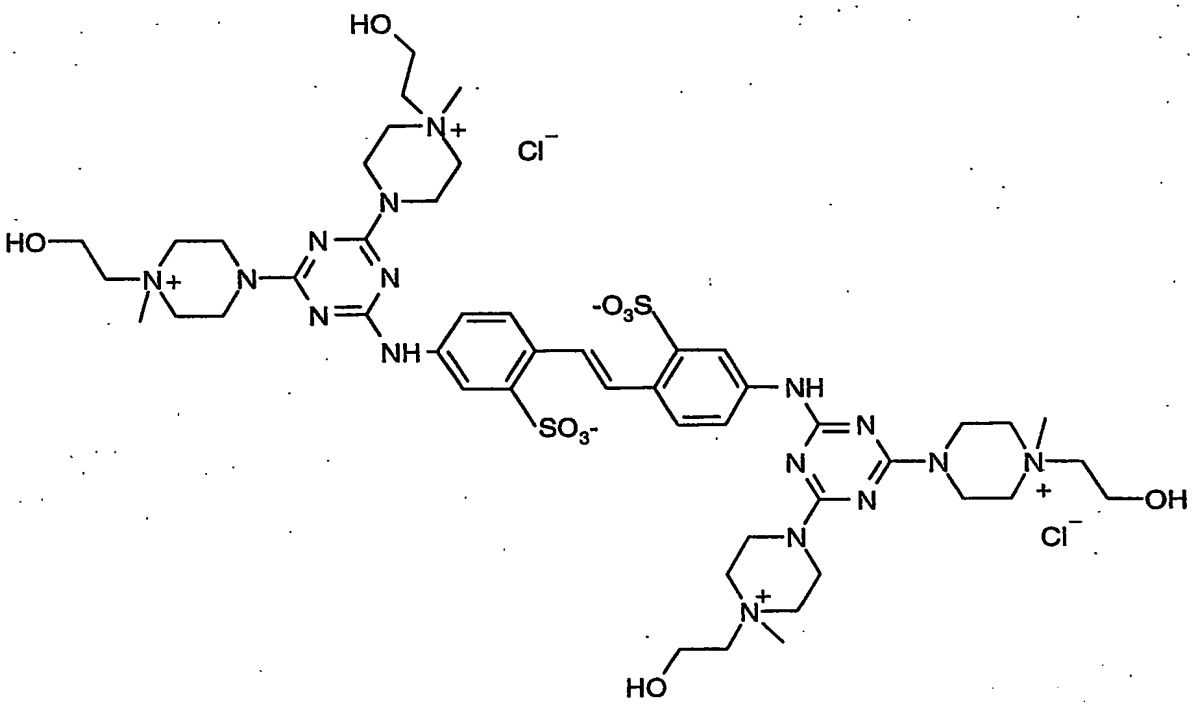
Example 12



(112)

By following the procedure described in Example 11, but replacing the compound of formula (110) by the compound of formula (107), the compound of formula (112) is obtained.

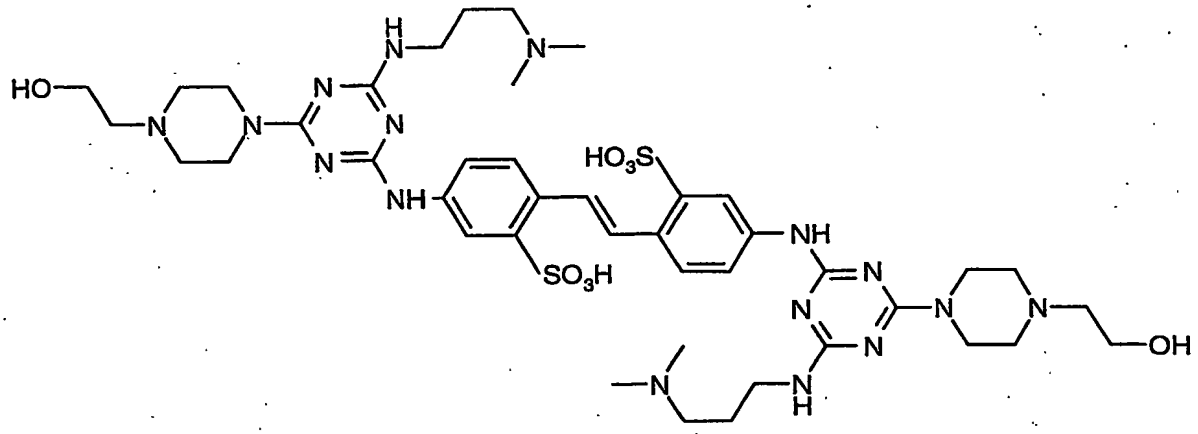
Example 13



(113)

33.0g of the compound of formula (112) is suspended in 200ml of an aqueous solution containing 10g of sodium chloride per 100ml of solution at room temperature and the pH adjusted to 1 by addition of concentrated hydrochloric acid. The pH is then raised to 5.5 by addition of aqueous sodium hydroxide solution and the resulting suspension stirred for a further 2 hours. The solids are filtered, washed with 10% aqueous sodium chloride solution and dried under vacuum at 70°C. There are obtained 28g of the compound of formula (113).

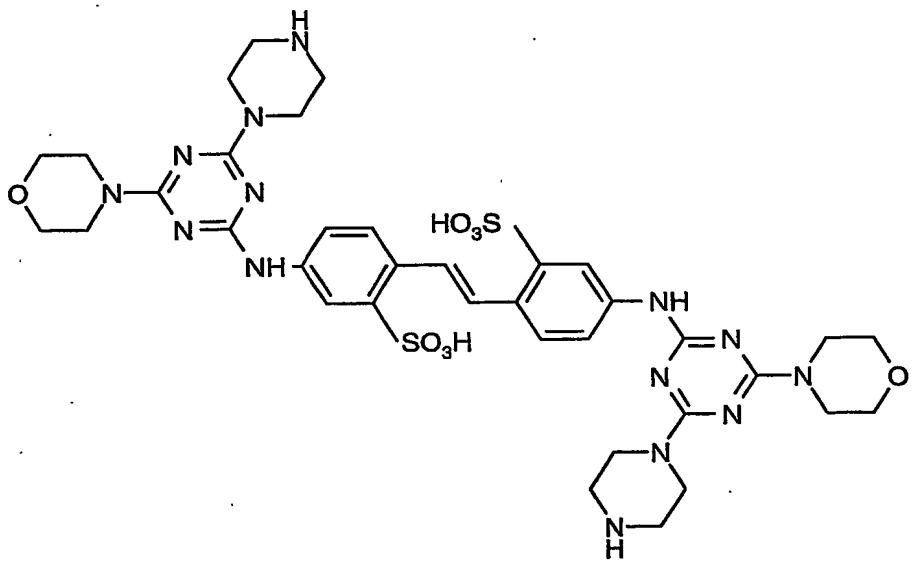
Example 14



(114)

By following the procedure described in Example 10, but replacing the N-methylpiperazine by an equivalent quantity of 3-dimethylamino-n-propylamine, there are obtained 11.4g of the compound of formula (114) as a yellow powder.

Example 15

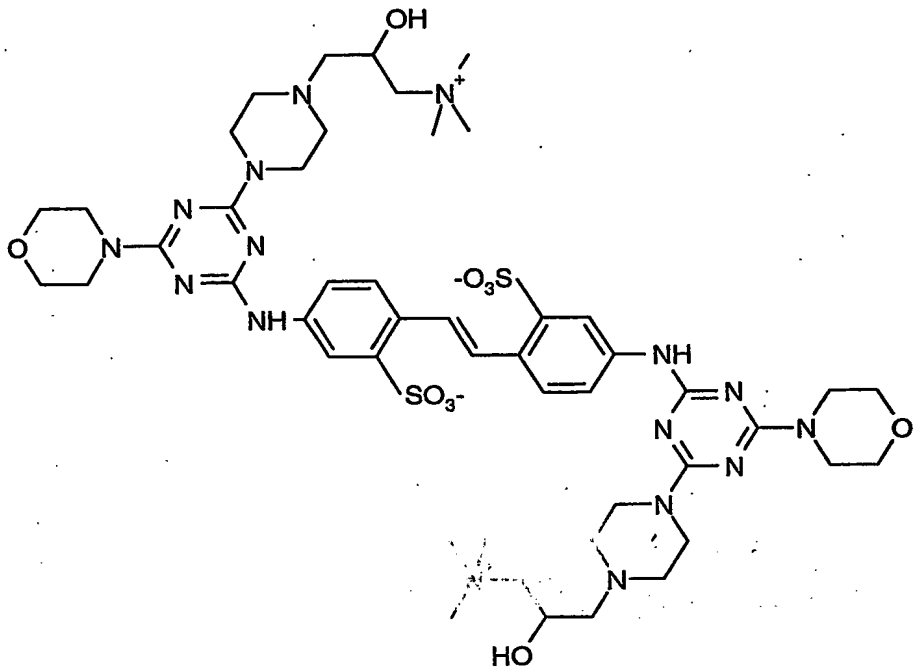


(115)

By following the procedure described in Example 5, but replacing the 4,4'-bis [(4-p-sulphonamidoanilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt by an equivalent quantity of 4,4'-bis [(4-N-morpholino-6-chloro-1,3,5-triazin-2-

yl)amino]stilbene-2,2'-disulphonic acid disodium salt, the compound of formula (115) is obtained.

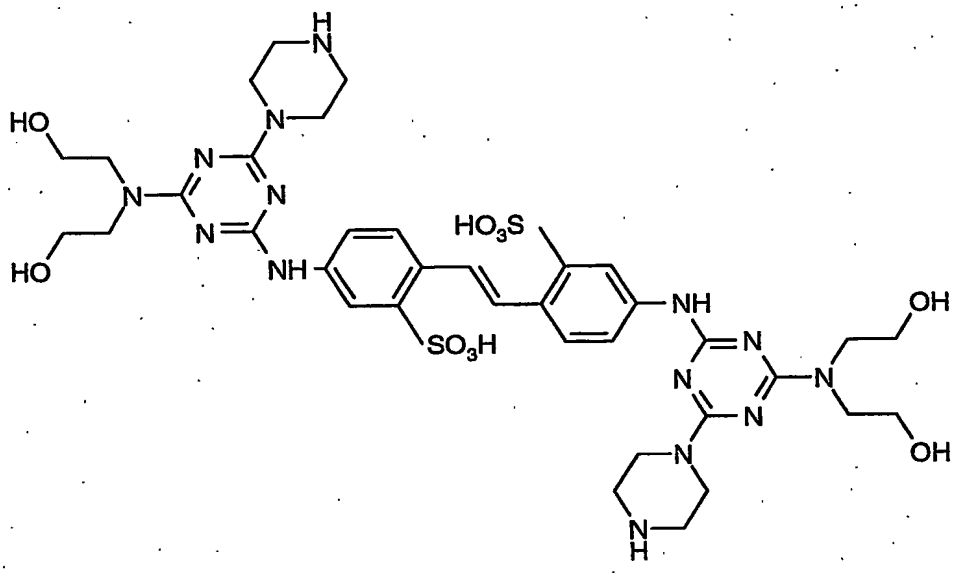
Example 16



(116)

8.67g of the compound of formula (115) are dissolved in 80ml of water and 20ml of 2N aqueous sodium hydroxide solution at 50°C. To this solution are then added 5.78g of 65% (3-chloro-2-hydroxypropyl)trimethylammonium chloride over 2 minutes and the mixture stirred for 90 minutes at 50°C. A further 0.58g of 65% (3-chloro-2-hydroxypropyl)-trimethylammonium chloride are then added, stirring continued for 60 minutes, the mixture again treated with 0.58g of 65% (3-chloro-2-hydroxypropyl)- trimethylammonium chloride, stirred for another 50 minutes at 50°C, the mixture cooled and stirring discontinued. After the solids have settled, the supernatant liquid is decanted and the white residue suspended in 100ml of water. The pH is first adjusted to 3.5 by addition of concentrated hydrochloric acid and then raised to 9.0 by addition of 2N aqueous sodium hydroxide solution. The precipitate is filtered, the residue slurried 3 times in water and, after the final filtration, dried under vacuum at 70°C. There are obtained 9.6g of the compound of formula (116) as yellow crystals.

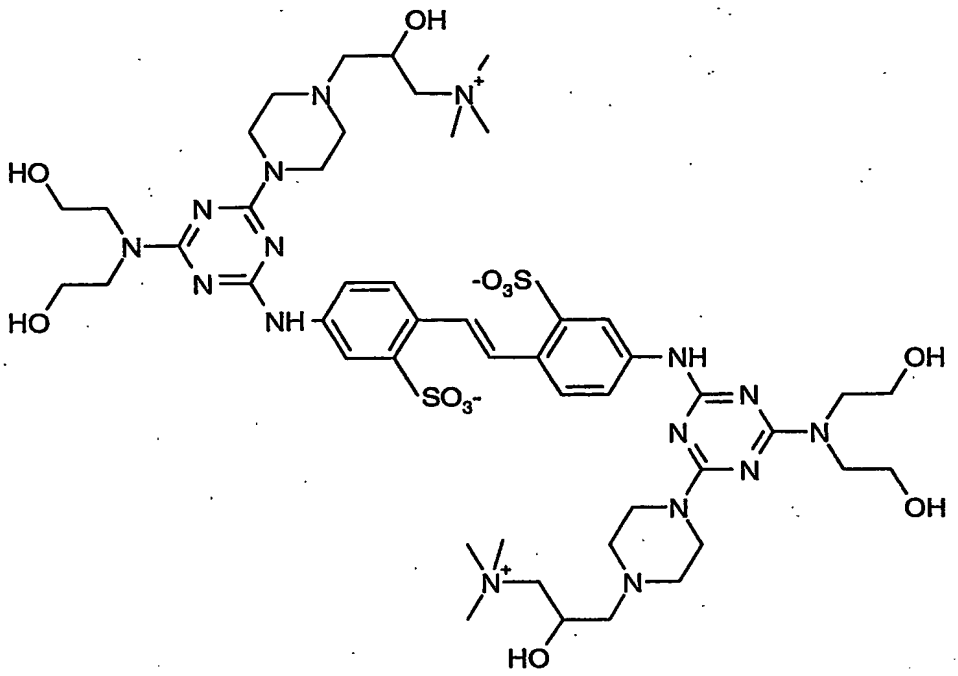
Example 17



(117)

By following the procedure described in Example 5, but replacing the 4,4'-bis [(4-p-sulphonanilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt by an equivalent quantity of 4,4'-bis [(4-diethanolamino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt, the compound of formula (117) is obtained as a fine yellowish powder.

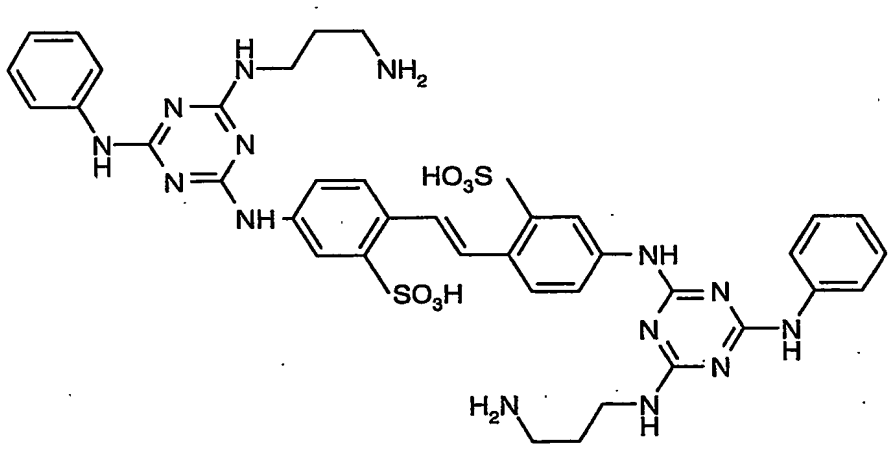
Example 18



(118)

By following the procedure described in Example 16, but replacing the compound of formula (115) by an equivalent quantity of the compound of formula (117), the compound of formula (118) is obtained as a yellowish powder.

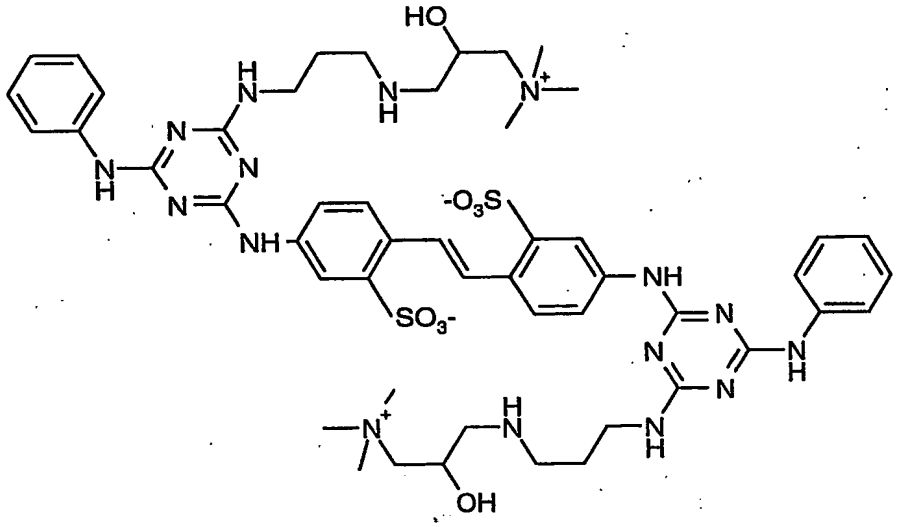
Example 19



(119)

By following the procedure described in Example 1, but replacing the 1-methylpiperazine by an equivalent quantity of 1,3-diamino-n-propane, the compound of formula (119) is obtained as yellow crystals.

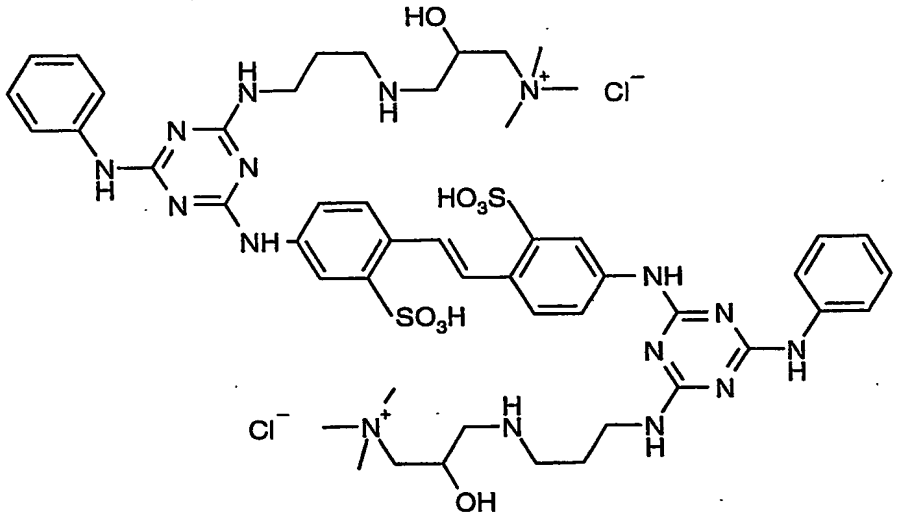
Example 20



(120)

By following the procedure described in Example 16, but replacing the compound of formula (115) by an equivalent quantity the compound of formula (119), the compound of formula (120) is obtained as yellow crystals.

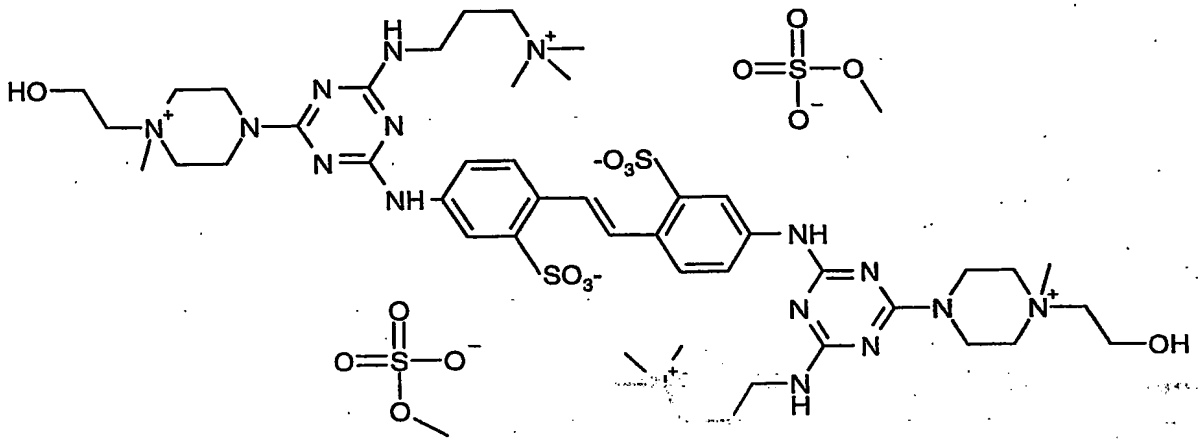
Example 21



(121)

By following the procedure described in Example 16, but replacing the compound of formula (115) by an equivalent quantity the compound of formula (119) and finally adjusting the pH to 4 by addition of concentrated hydrochloric acid, the compound of formula (121) is obtained as yellow crystals.

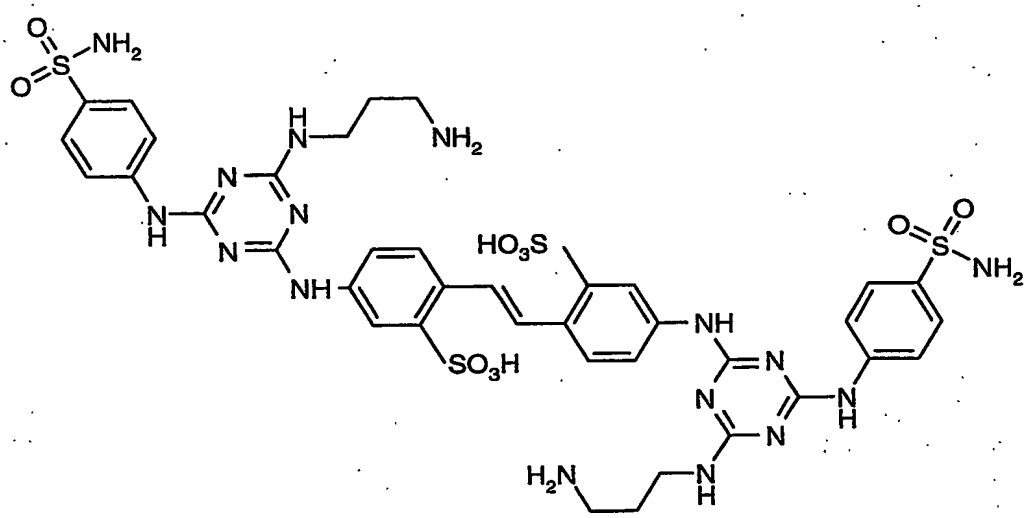
Example 22



(122)

5.0g of the compound of formula (114) are added to 50ml of water and 7.5ml of 2N aqueous sodium hydroxide solution and warmed to 45°C when a yellow solution results. The solution is cooled to 35°C and rapidly treated with 3.8g of dimethyl sulphate. After stirring for 4.5 hours at 35°C, during which time the pH is maintained at 9.0 by addition of a total of 5ml of 2N aqueous sodium hydroxide solution, the temperature is raised to 60°C and the mixture stirred for a further 1 hour. The mixture is then evaporated on a rotary evaporator and the residue dried under vacuum at 70°C. There are obtained 8.9g of the compound of formula (122) as yellow crystals.

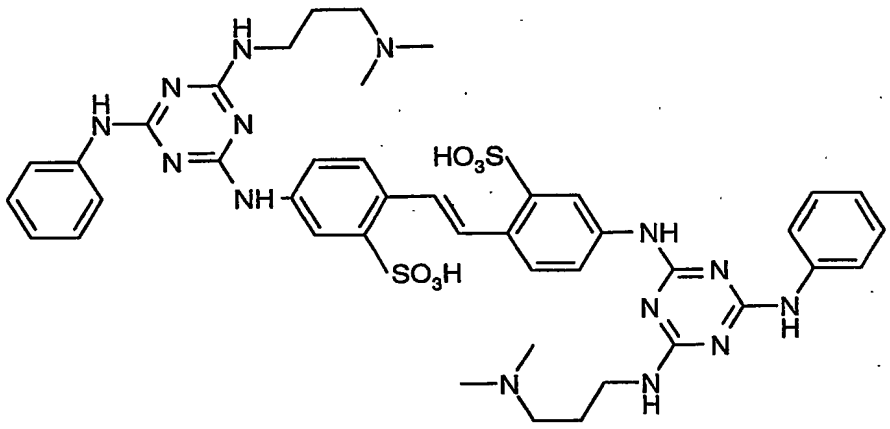
Example 23



(123)

By following the procedure described in Example 5, but replacing the piperazine by an equivalent quantity of 1,3-diaminopropane, the compound of formula (123) is obtained as brownish crystals.

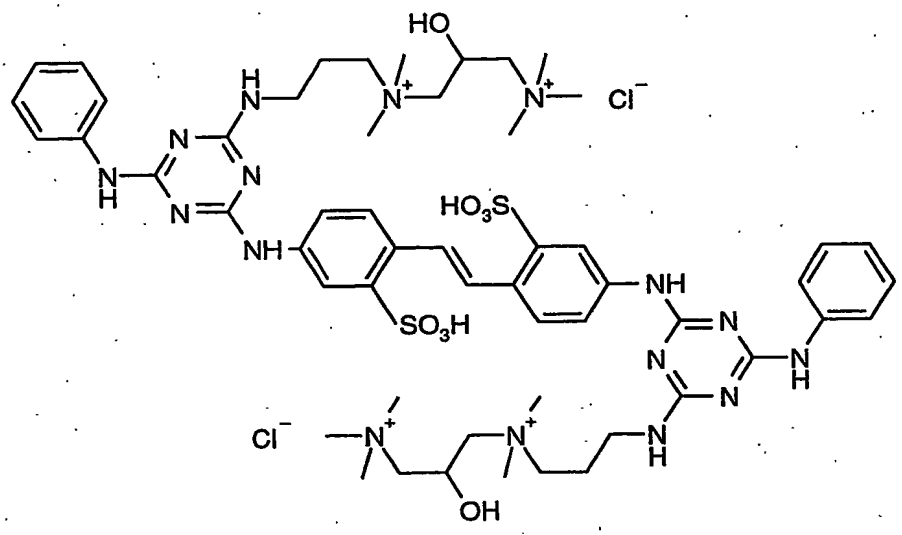
Example 24



(124)

By following the procedure described in Example 1, but replacing the 1-methylpiperazine by an equivalent quantity of 3-N,N'-dimethylamino-1-propylamine, the compound of formula (124) is obtained.

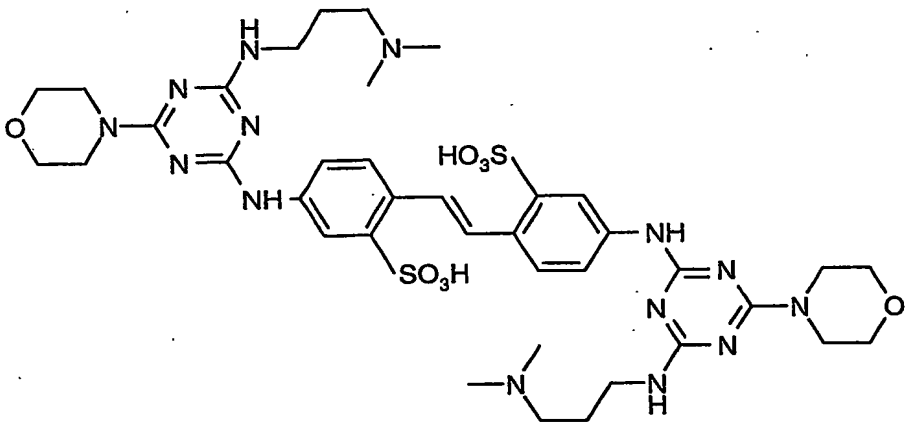
Example 25



(125)

By following the procedure described in Example 16, but replacing the compound of formula (115) by an equivalent quantity of the compound of formula (124), the compound of formula (125) is obtained as a yellowish solid.

Example 26

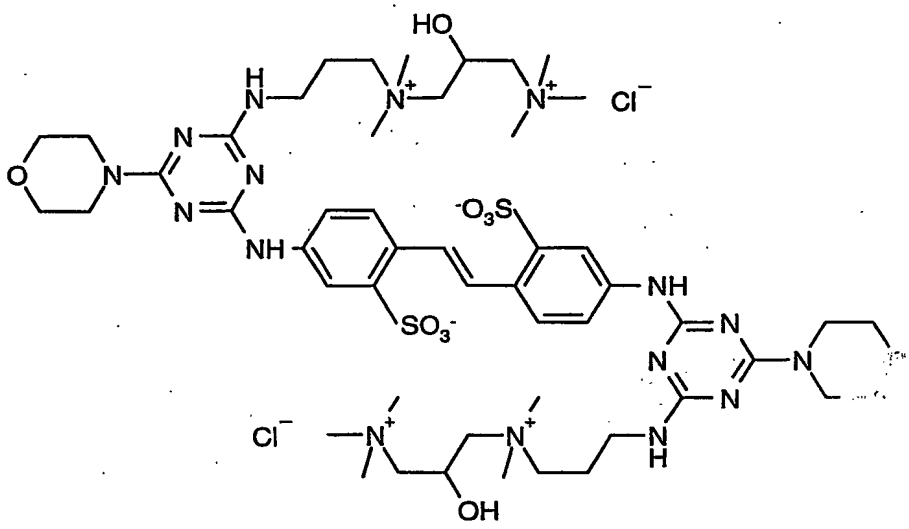


(126)

150g of 4,4'-bis [(4-N-morpholino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt with an active content of 91% are added in portions with stirring at 25°C to 350ml of 3-N,N'-dimethylamino-1-propylamine. During the addition, the temperature is raised to 90°C within 10 minutes and, during the following 10 minutes, further increased to 100°C

and the mixture maintained at this temperature for a further 1 hour. Heating is then ceased and the mixture diluted with 250ml of water and evaporated under vacuum. The resulting syrup is stirred with 170ml of concentrated hydrochloric acid for 1 hour at 25°C and the precipitated solids filtered with suction and dried under vacuum at 70°C. There are obtained 142g of the compound of formula (126).

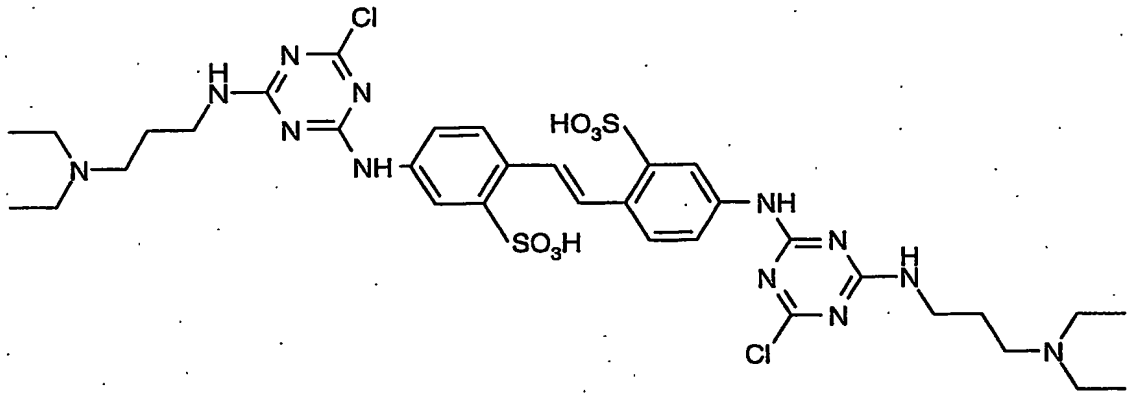
Example 27



(127)

By following the procedure described in Example 16, but replacing the compound of formula (115) by an equivalent quantity of the compound of formula (126), the compound of formula (127) is obtained as a yellow solid.

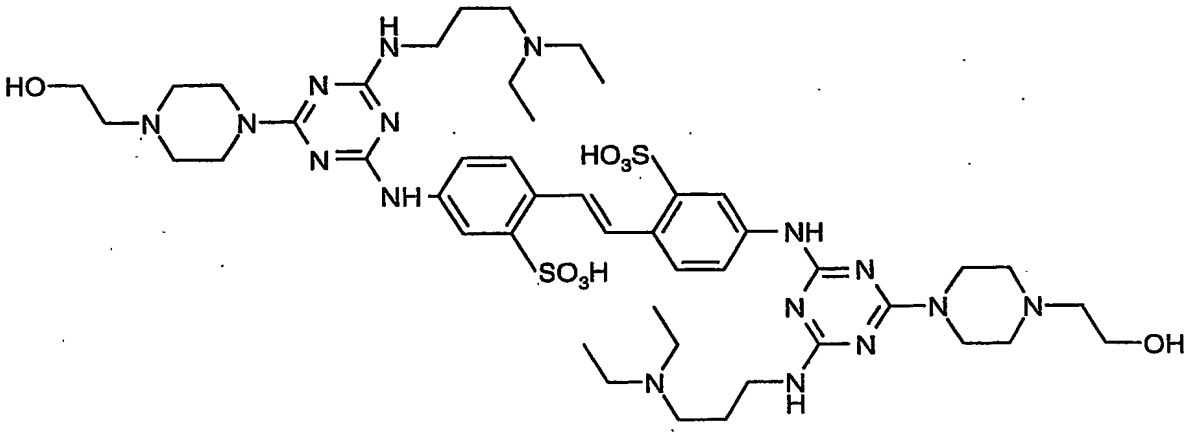
Example 28



(128)

By following the procedure described in Example 6, but replacing the N-(2-hydroxyethyl)-piperazine by an equivalent quantity of 3-diethylamino propylamine, 263.7g of the compound of formula (128) are obtained as yellow crystals.

Example 29

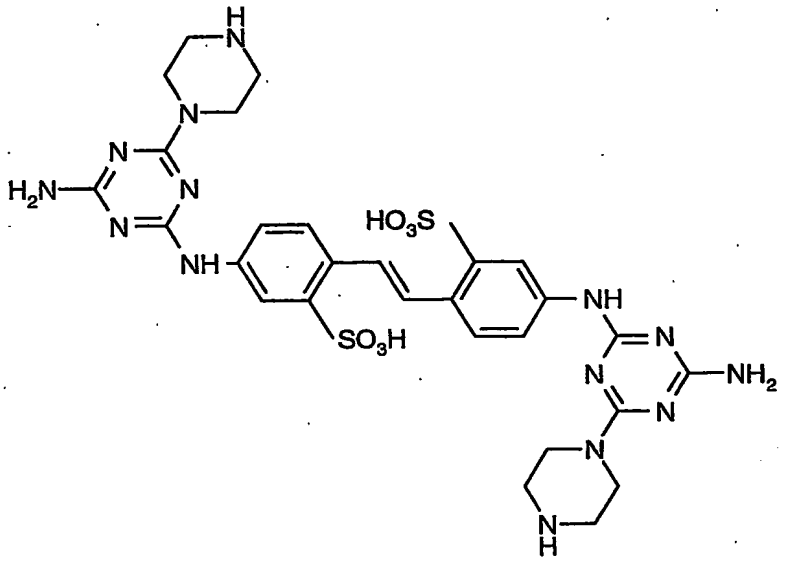


(129

30.0g of the compound of formula (128) are added to 70ml of water, the pH adjusted to 10.6 by addition of 4N aqueous sodium hydroxide solution and the mixture heated to 70°C, when solution results. To this solution, 21.9g of 1-(2-hydroxyethyl)piperazine are added at 70-75°C, the temperature is raised to 96°C and the solution stirred for a total of 3 hours at this temperature. After cooling to 70°C, the pH is adjusted to 4.5 with concentrated hydrochloric acid, when an oil separates. The residue, after decantation of the aqueous liquors, is treated with 400ml of water and allowed to stand. 10g of sodium chloride are added and the solids

separated by filtration, washed with 10% brine and dried under vacuum at 70°C. There are obtained 15.8g of the compound of formula (129) as yellow crystals.

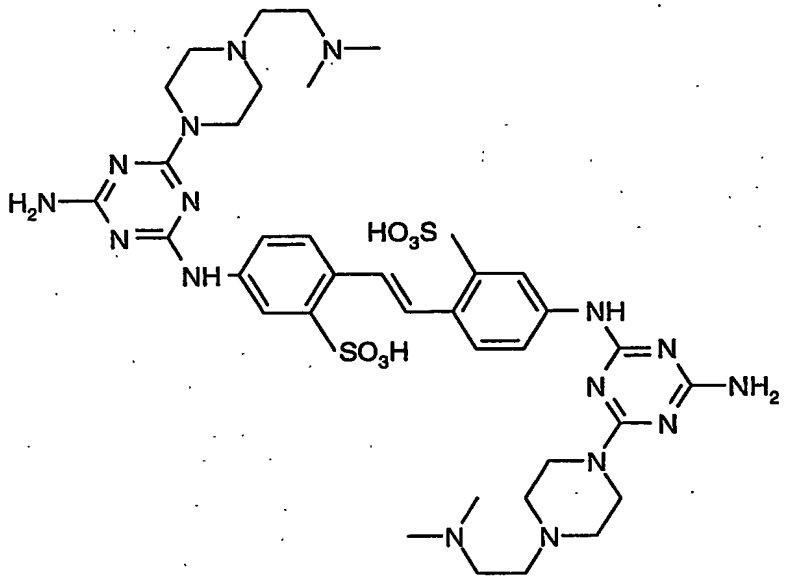
Example 30



(130)

To 58.4g of piperazine in a mixture of dioxan and 150ml of water, previously heated to 70-75°C, are added 40g of 4,4'-bis [(4-amino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt with stirring. The temperature is raised to 80-85°C and the yellowish brown solution stirred for 2 hours. The pH is adjusted to 4.5 by addition of 100ml of concentrated hydrochloric acid, the mixture cooled to 20°C and the precipitated solids filtered. After suspension in water, dissolution at pH 11 and reprecipitation with concentrated hydrochloric acid at pH 4.5, the filtered solids are washed with water and dried under vacuum at 70°C. There are obtained 20.0g of the compound of formula (130) as yellow crystals.

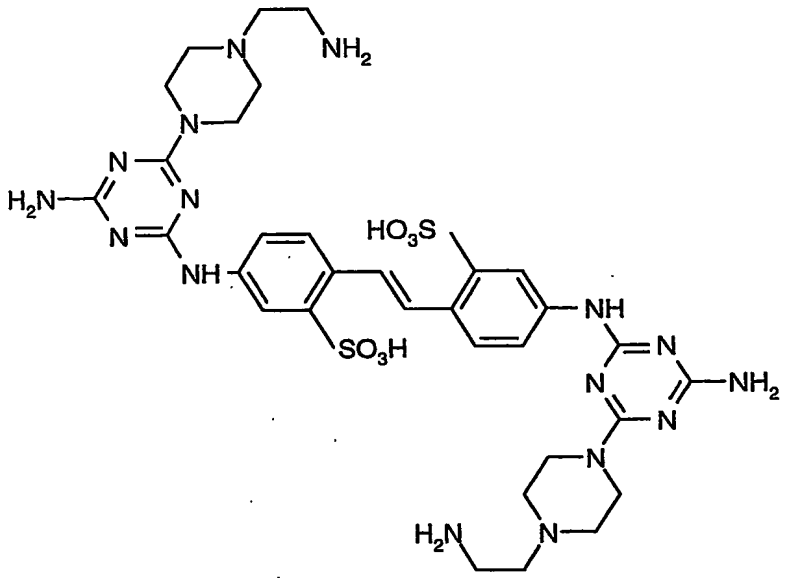
Example 31



(131)

Proceeding essentially as described in Example 30, but replacing the piperazine by an equivalent quantity of 1-(2-dimethylaminoethyl)piperazine, the compound of formula (131) is obtained as yellow crystals.

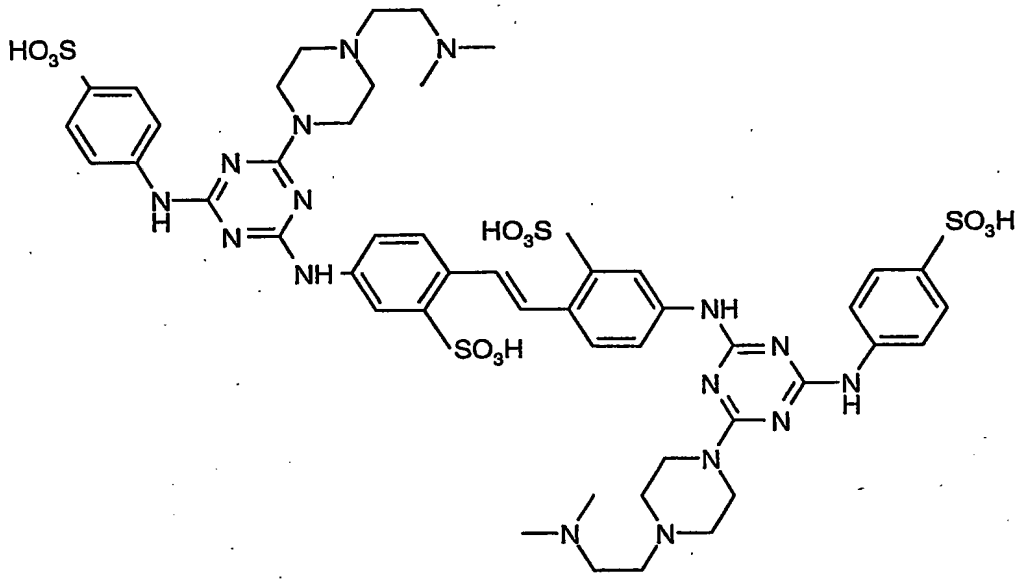
Example 32



(132)

By proceeding essentially as described in Example 30, but replacing the piperazine by an equivalent quantity of 1-(2-aminoethyl)piperazine, the compound of formula (132) is obtained as yellow crystals.

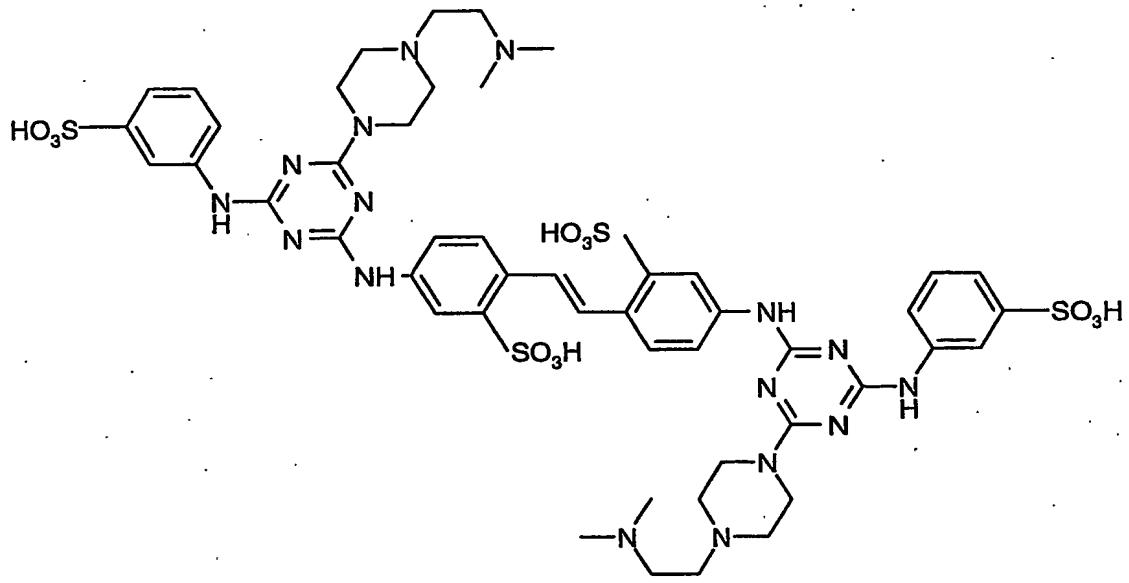
Example 33



(133)

25.0g of 4,4'-bis [(4-p-sulphoanilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid tetra sodium salt are dissolved in 150ml of water and 8.2g of 1-(2-dimethylaminoethyl)-piperazine added. The temperature is raised to 96°C and the yellow solution stirred for 3 hours at this temperature, the pH being maintained at 8.3 by addition of 2N aqueous sodium hydroxide solution. After cooling to 70°C, the pH is adjusted to 4.5 by addition of 8ml of concentrated hydrochloric acid and the mixture stirred for 1 hour. The precipitated solids are filtered, suspended in 250ml of water and dissolved by addition of sodium hydroxide solution to pH 8.5. Stirring is continued for 2 hours, after which time the pH is adjusted to 4.0 with concentrated hydrochloric acid, the solids filtered, washed with water and dried under vacuum at 70°C. There are obtained 25.5g of the compound of formula (133) as yellow crystals.

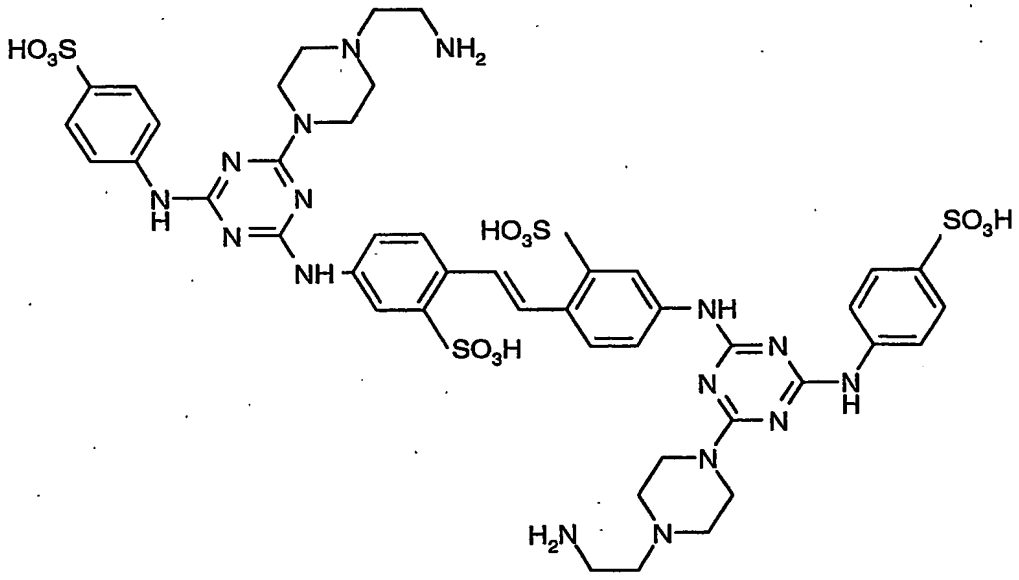
Example 34



(134)

By following the procedure described in Example 33 but replacing the 4,4'-bis [(4-p-sulphoanilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid tetra sodium salt by 4,4'-bis [(4-m-sulphoanilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid tetra sodium salt, 23.9g of the compound of formula (134) are obtained as yellow crystals.

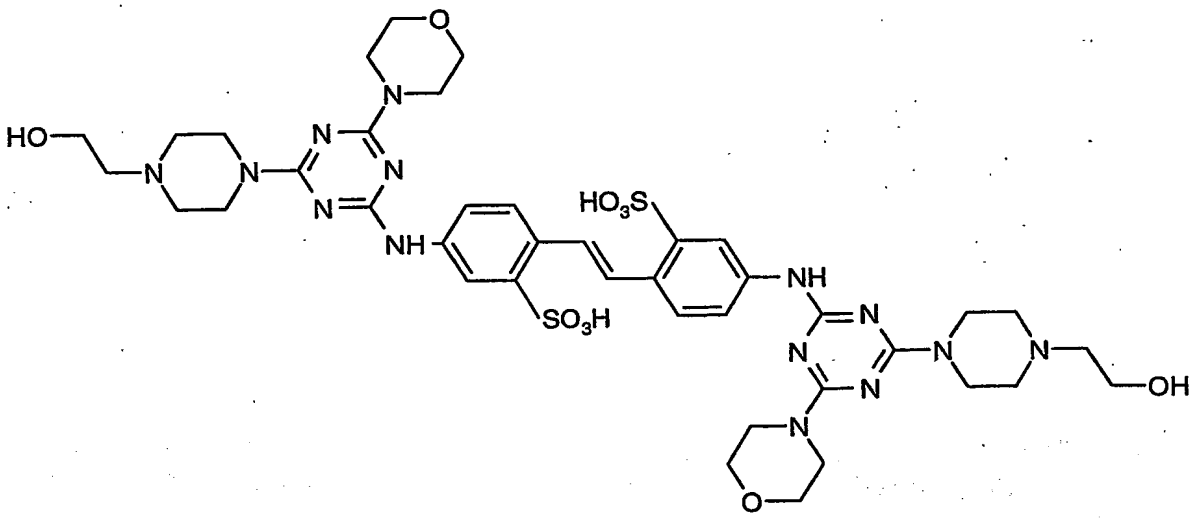
Example 35



(135)

By following the procedure described in Example 33, but replacing the 1-(2-dimethylaminoethyl)-piperazine by an equivalent quantity of 1-(2-aminoethyl)piperazin, 23.8g of the compound of formula (135) are obtained as yellow crystals.

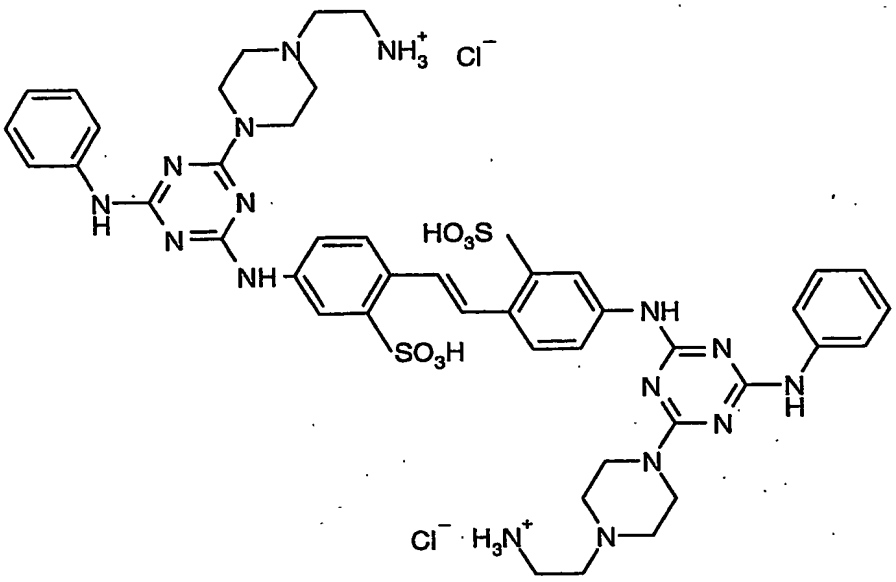
Example 36



(136)

By following the procedure described in Example 7, but replacing the N-(2-hydroxyethyl)-piperazine by an equivalent quantity of morpholine, there are obtained 304.9g of the compound of formula (136) as yellow crystals.

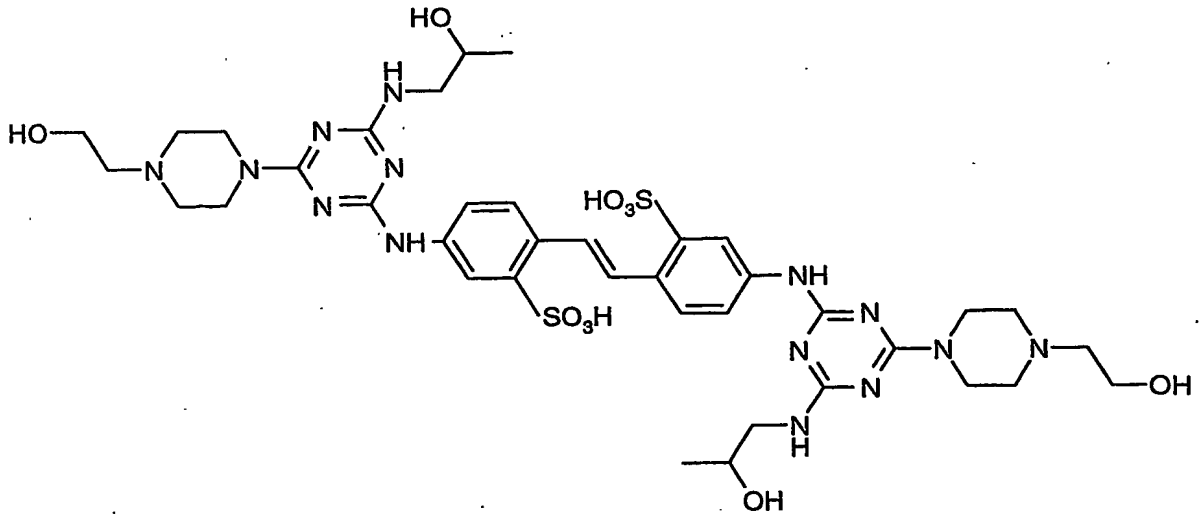
Example 37



(137)

Following the procedure described in Example 30, but replacing the piperazine by an equivalent quantity of 1-(2-aminoethyl)piperazine and the 4,4'-bis [(4-amino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt by an equivalent quantity of 4,4'-bis [(4-anilino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt, 40.3g of the compound of formula (137) are obtained as yellow crystals.

Example 38

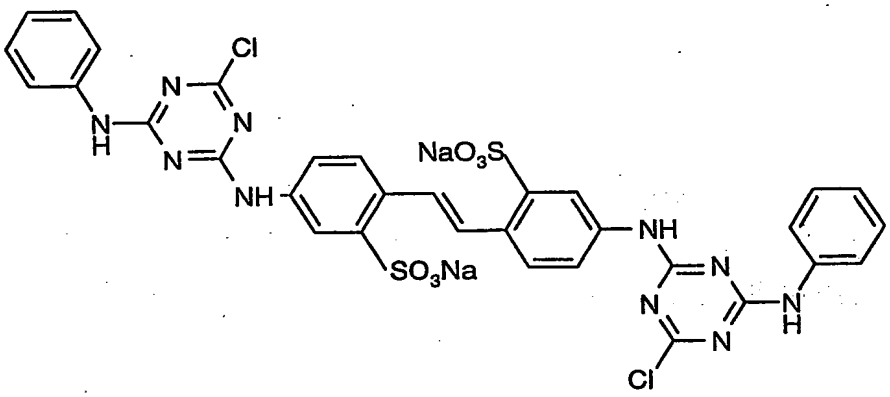


(138

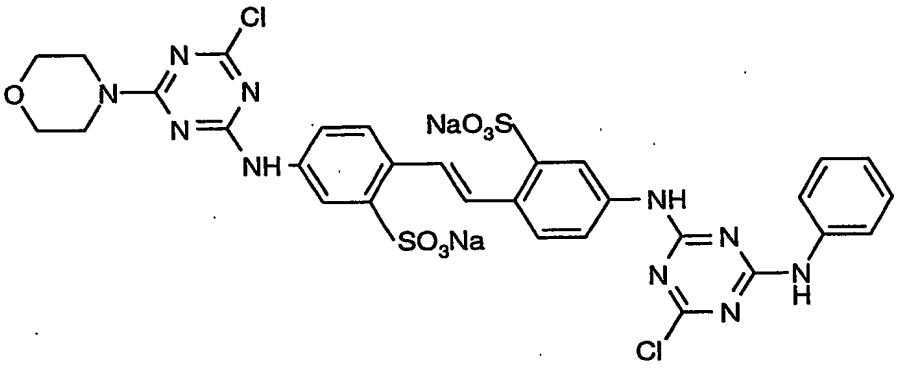
By following the procedure described in Example 30, but replacing the piperazine by an equivalent quantity of 1-(2-hydroxyethyl)piperazine and the 4,4'-bis [(4-amino-6-chloro-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid disodium salt by an equivalent quantity of 4,4'-bis {[4-(2-hydroxy)propylamino-6-chloro-1,3,5-triazin-2-yl]amino}stilbene-2,2'-disulphonic acid disodium salt (see Example 41), 36.8g of the compound of formula (138) are obtained as yellow crystals.

Example 39

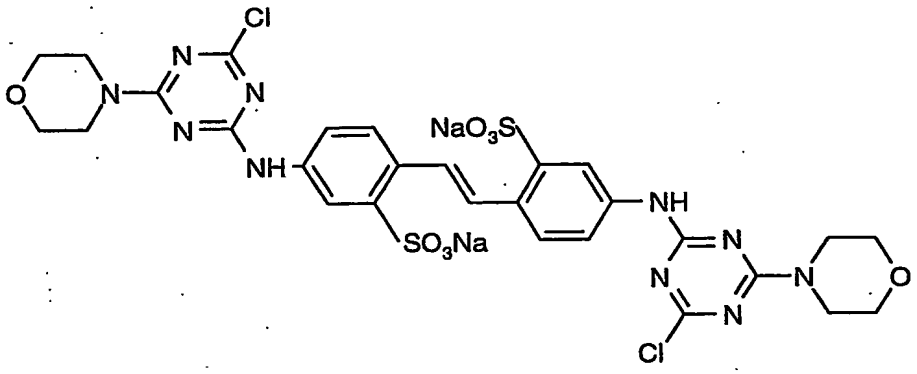
A mixture of compounds of formulae



(139a)



(139b) and

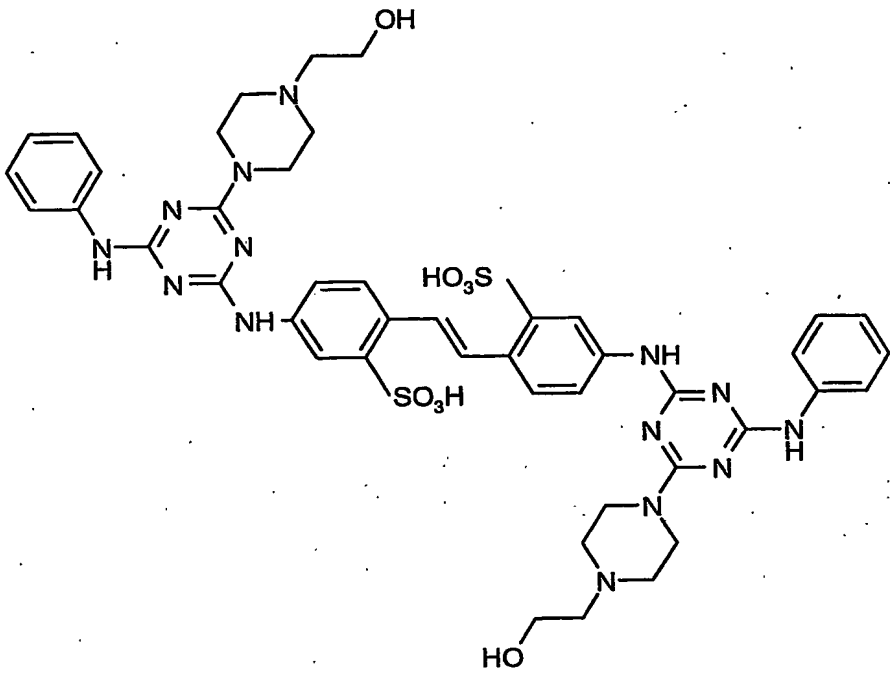


(139c)

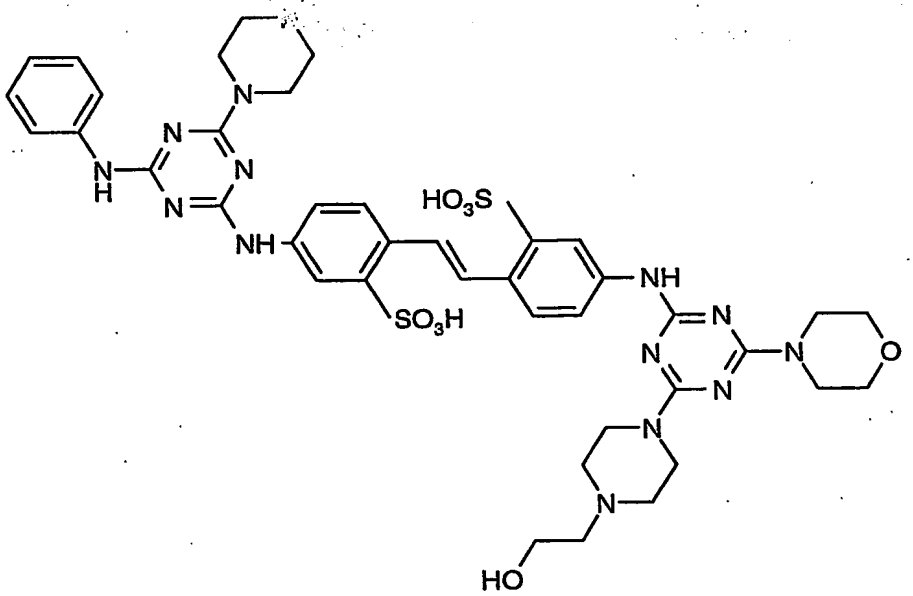
A solution of 120g of cyanuric chloride in 930ml of methyl ethyl ketone is added with stirring over 10 minutes at 5-10°C to 400g of ice/water. Then, during 70 minutes at a pH of from 4.5 to 5.0, 1093g of a 12% solution of 4,4'-diaminostilbene-2,2'-disulphonic acid and sodium carbonate are added such that no excess of 4,4'-diaminostilbene-2,2'-disulphonic acid is present. The mixture is stirred for a further 10 minutes at 5-10°C, after which time a total of 21.2ml of 20% aqueous sodium carbonate solution is consumed. The mixture is warmed to 8-20°C and the pH adjusted to 7.5 by addition of 50% aqueous sodium hydroxide solution. A mixture of 29.9g of aniline and 28.0g of morpholine is added dropwise over 10 minutes, the mixture warmed to 70°C during 60 minutes and stirring continued for 90 minutes at this temperature, the methyl ethyl ketone being distilled off. A total of 54.2ml of 50% aqueous sodium hydroxide solution are required to maintain a pH of 7.5 during this period. The reaction mixture is then cooled to 30°C over 60 minutes and allowed to stand overnight at room temperature. The supernatant liquid is decanted off, the residue suspended in 750ml of 5% brine, warmed to 60°C and then slowly cooled to 30°C over 60 minutes. The precipitated solids are filtered, washed with 5% brine and dried under vacuum at 70°C. There are obtained 259.1g of a yellow crystalline product containing 27% of the compound of formula (139a), 46% (139b) and 24% (139c).

Example 40

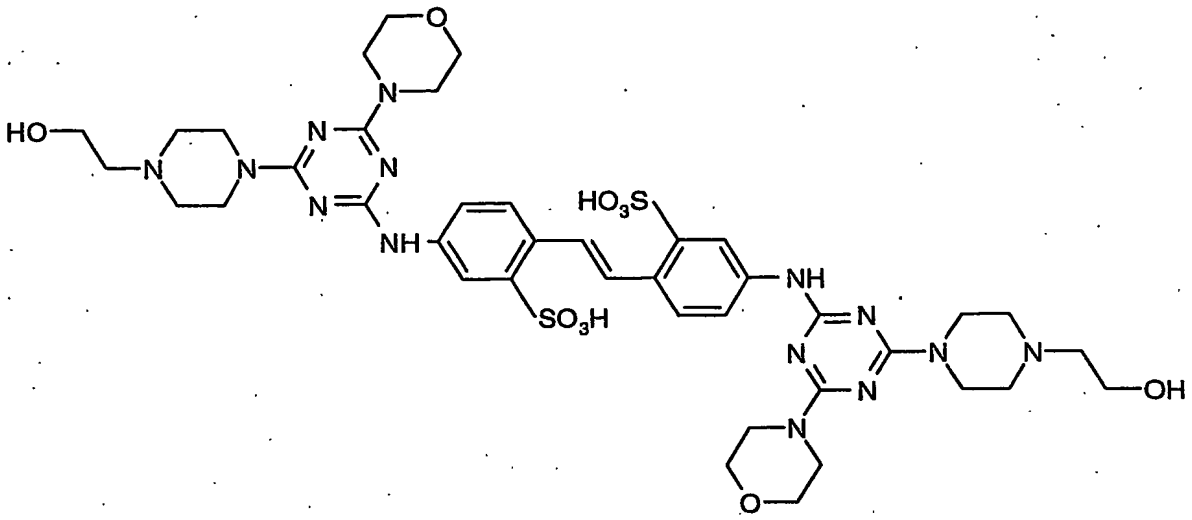
A mixture of compounds of formulae



(102),



(140) and

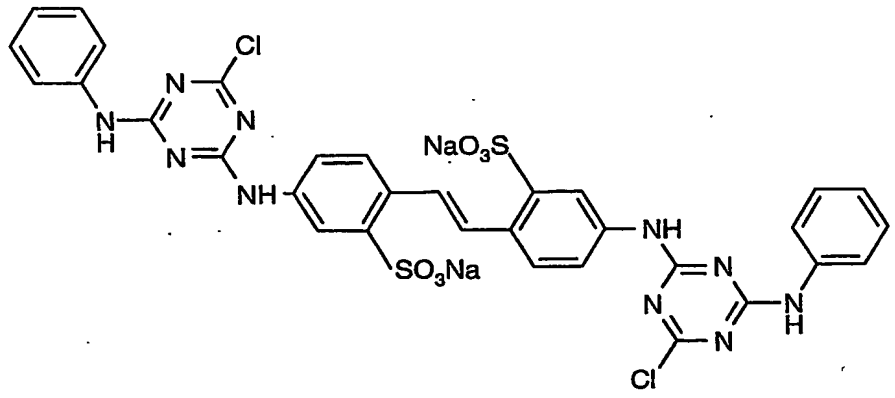


(136

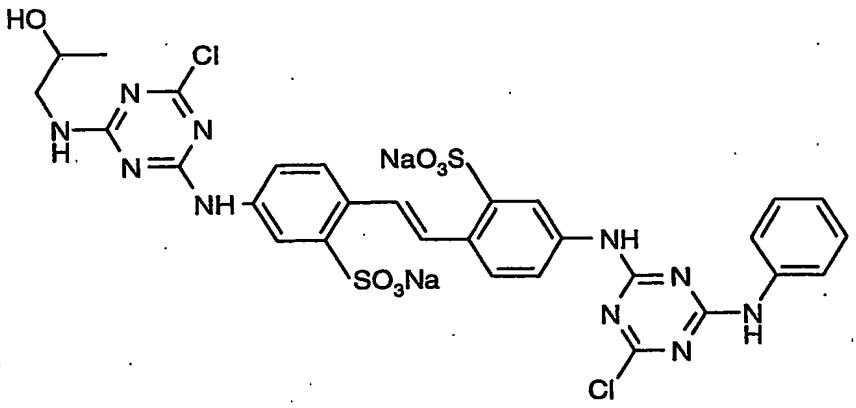
A mixture of 150ml of water, 150ml of dioxan and 55.7g of 1-(2-hydroxyethyl)piperazine is stirred and heated to 70-75°C and 35.0g of the mixture of compounds (139a), (139b) and (139c), obtained as described in Example 39, added over 1 hour. The temperature is increased to 86-88°C and the mixture stirred for a further 4 hours. After cooling to 70°C, 60ml of concentrated hydrochloric acid are added to pH 4.0 and the mixture further cooled to 20°C. Addition of 300ml of 5% brine results in precipitation; the solids are filtered, washed with 5% brine and dried under vacuum at 70°. There are obtained 26.6g of a yellow solid consisting of a mixture of 34% of compound (102), 44% of compound (140) and15% of compound (136).

Example 41

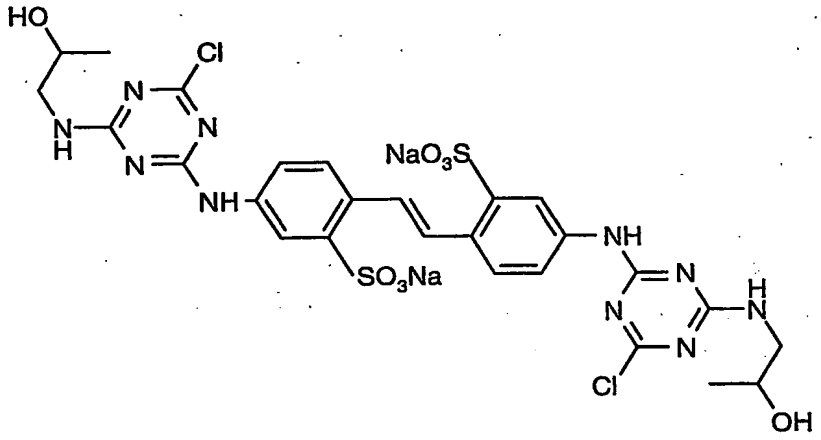
A mixture of compounds of formulae



(139a),



(141a) and

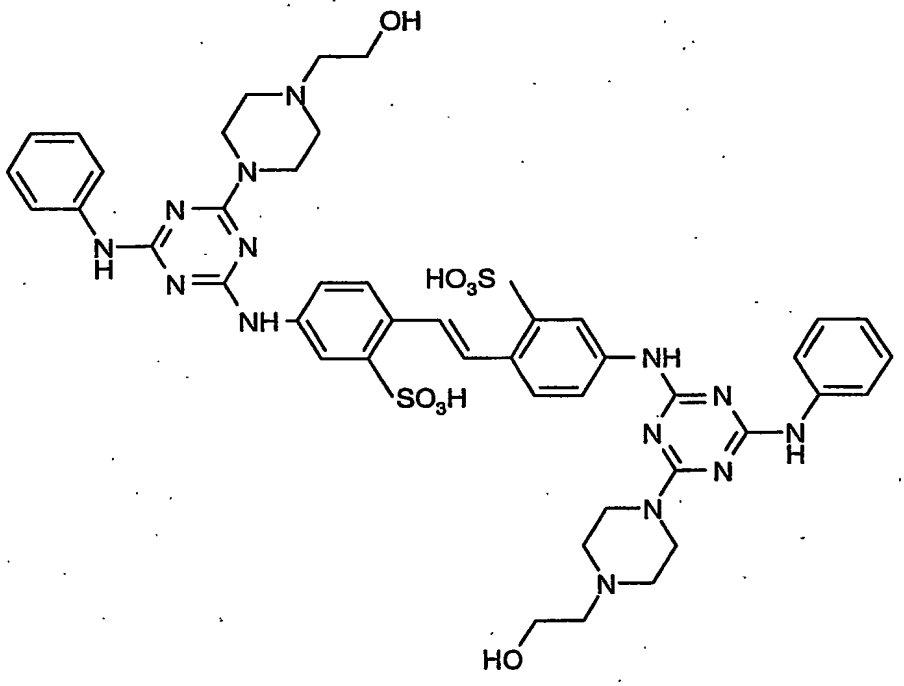


(141b)

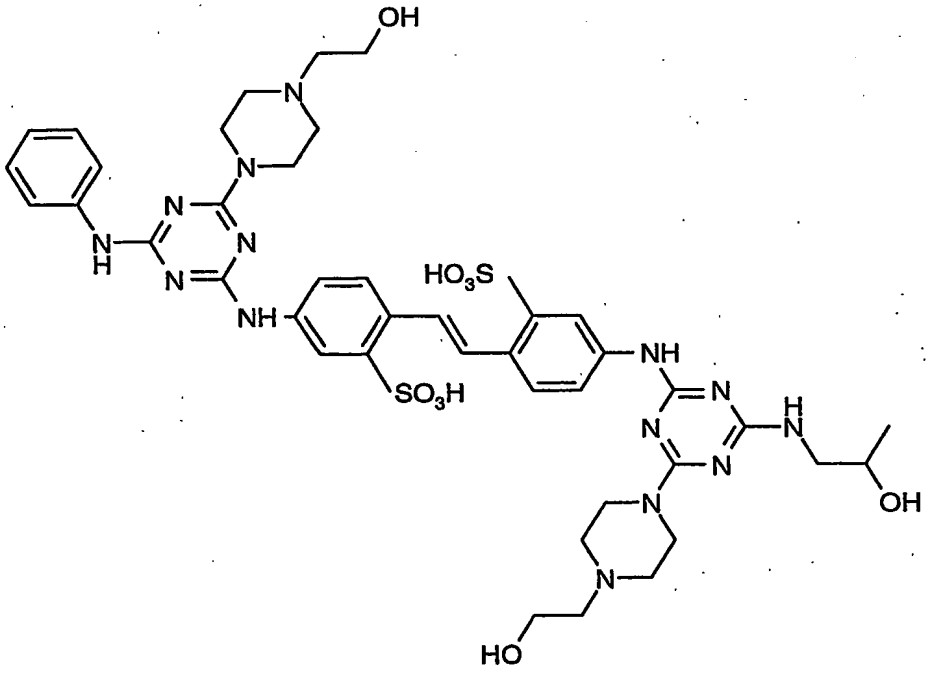
By following the procedure described in Example139, but replacing the morpholine by an equivalent quantity of 1-aminopropan-2-ol, 188.5g of a mixture of compounds containing 33% of the compound of formula (139a), 40% (141a) and 23% (141b) is obtained, as yellow crystals.

Example 42

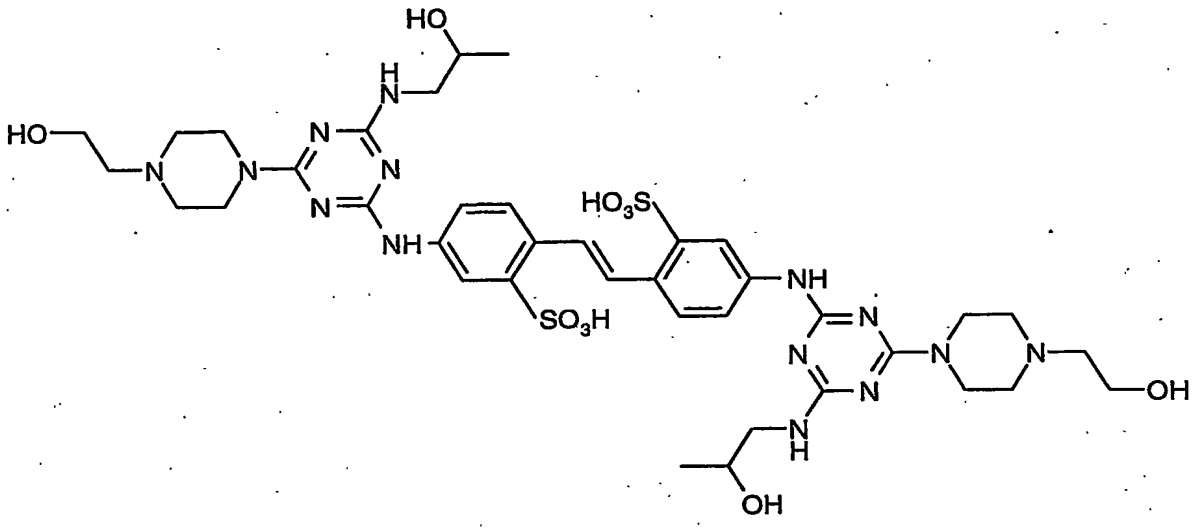
A mixture of compounds of formulae



(102),



(142) and



(138)

By following the procedure described in Example 40, but replacing the mixture of compounds (139a), (139b) and (139c), obtained as described in Example 39, by an equivalent quantity of the mixture of compounds of formula (139a), (141a) and (141b) of Example 40, there are obtained 35.4g of yellow crystalline solids containing 35% of the compound of formula (102), 39% (142) and 20% (138).

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